P & TM Agribusiness CP 2.01

22. März 2001

APPL. [redacted] INDUE [redacted] PCT

CC:

PATENT COOPERATION TREATY

1H

WO 01/17351
PCT/EP00/08658

From the INTERNATIONAL BUREAU

To:
SYNGENTA PARTICIPATIONS AG
Intellectual Property
P.O. Box
CH-4002 Basel
SUISSE

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

Date of mailing (day/month/year) 15 March 2001 (15.03.01)		
Applicant's or agent's file reference EPH/5-31140A		**IMPORTANT NOTICE**
International application No. PCT/EP00/08658 ✓	**International filing date** (day/month/year) 05 September 2000 (05.09.00)	**Priority date** (day/month/year) 07 September 1999 (07.09.99)
Applicant SYNGENTA PARTICIPATIONS AG et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
   AU,KP,KR,US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
   AE,AG,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,BZ,CA,CH,CN,CR,CU,CZ,DE,DK,DM,DZ,EA,EE,EP,ES,
   FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,
   MN,MW,MX,MZ,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,
   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
   15 March 2001 (15.03.01) under No. WO 01/17351

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, **a demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume I of the PCT Applicant's Guide.

DATA ENTERED
23 MRZ 2001
DATE: VISUM:

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

Form PCT/IB/308 (July 1996)

3883255

Copy for the Elected Office (EO/US)

PCT/EP00/08658

P, ENT COOPERATION TREA.

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

SYNGENTA PARTICIPATIONS AG
Intellectual Property
P.O. Box
CH-4002 Basel
SUISSE

Date of mailing (day/month/year)
29 January 2002 (29.01.02)

IMPORTANT NOTIFICATION

Applicant's or agent's file reference
PH/5-31140A

International application No.
PCT/EP00/08658

International filing date (day/month/year)
05 September 2000 (05.09.00)

1. The following indications appeared on record concerning:

[X] the applicant [X] the inventor [ ] the agent [ ] the common representative

Name and Address
FRIEDMANN, Adrian, Alberto
Hebelstrasse 95
CH-4056 Basel
Switzerland

State of Nationality: CH
State of Residence: CH
Telephone No.:
Facsimile No.:
Teleprinter No.:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [ ] the name [X] the address [ ] the nationality [X] the residence

Name and Address
FRIEDMANN, Adrian, Alberto
41 South View Avenue
Caversham
Reading RG4 5AD
United Kingdom

State of Nationality: CH
State of Residence: GB
Telephone No.:
Facsimile No.:
Teleprinter No.:

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[ ] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer
Dominique DELMAS

Telephone No.: (41-22) 338.83.38

P. ENT COOPERATION TREA.

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 18 May 2001 (18.05.01)	
International application No. PCT/EP00/08658	**Applicant's or agent's file reference** PH/5-31140A
International filing date (day/month/year) 05 September 2000 (05.09.00)	**Priority date** (day/month/year) 07 September 1999 (07.09.99)
Applicant GLOCK, Jutta et al	

1. The designated Office is hereby notified of its election made:

   [X] in the demand filed with the International Preliminary Examining Authority on:

   23 March 2001 (23.03.01)

   [ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

   [ ] was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Juan Cruz

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

RECD 07 DEC 2001
WIPO PCT

12

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
PH/5 -31140A		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP00/08658	05/09/2000	07/09/1999
International Patent Classification (IPC) or national classification and IPC A01N43/90		
Applicant SYNGENTA PARTICIPATIONS AG et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☒ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
23/03/2001	05.12.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Krattinger, B Telephone No. +49 89 2399 8550

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/08658

I. Basis f th r p rt

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-45 as originally filed

Claims, No.:

1-7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-7
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-7
Industrial applicability (IA)	Yes:	Claims	1-7
	No:	Claims	

2. Citations and explanations
see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

R It m V

The present invention concerns compositions containing (a) a 3-hydroxy-4-aryl-5-oxopyrazoline of formula I and (b) a synergistic amount of different type of herbicides (claims 1-3) and methods of controlling weeds and grasses in crops (claims 4-7).

Reference is made to the following documents:

D1: WO 96 21652 A cited in the application
D2: EP-A-0 508 126
D3: DE 197 28 568 A

A. Since the different compounds given in (b) are not structurally related, they must possess different action pathways when used in combination with a 3-hydroxy-4-aryl-5-oxopyrazoline of formula I, so that it seems highly improbable that derivatives with so different structures would all lead to a synergistic combination when used with 3-hydroxy-4-aryl-5-oxopyrazoline of formula I. The description discloses only a few examples of synergism with only one derivative clofinafop (=phenoxy-phenoxypropionic acid; on pages 40-41). Considering the broad definition of claim 1 concerning the derivatives (b), the application does not meet the requirements of Art. 5 PCT because the description does not illustrate and demonstrate the synergistic effect for the different type of (b) ingredients : the application lacks sufficient disclosure, the onus of establishing that the invention may be performed over substantially the all claimed range lies with the Applicant.

Novelty

1. Document D1 discloses compounds of formula I but does not disclose synergistic composition containing a compound as defined in (b).

2. The presently claimed compositions are the result of several selections over the generic formulas defined in document D2 (selection for example, according to the formula of document D2, on X, Y, Z, n, etc.) and the choice of components (b). The specific compounds of document D2 falling within the scope of the formula I of D1 are not described in synergistic compositions.

3. None of the compounds of D3 possess the formula I.

4. Therefore in view of what is said above, it can be seen that the presently claimed matter is new (Art. 33(2) PCT).

Nevertheless the proviso concerning R1 and R3 looks like an exclusion performed in order to avoid prior art which is known to the Applicant. When the application enters the European Regional Phase, the Applicant will be invited to justify these exclusions. If they are due to a prior art, the Applicant will be invited to name it, and possibly to insert and comment its content in the description.

Inventive Step

Document D2 which is considered as closest prior art describe compositions containing a 3-hydroxy-4-aryl-5-oxopyrazoline and eventually others herbicides. The 3-hydroxy-4-aryl-5-oxopyrazoline of the present application are the result of a selection over the generic formula of the 3-hydroxy-4-aryl-5-oxopyrazoline of document D2. Document D2 states clearly on page 31, line 24-40 that combinations containing 3-hydroxy-4-aryl-5-oxopyrazoline and other herbicides such as azinones, triazinones, sulfonyureas, anilides, imidazolinones, dinitroanilines or carbamates lead to synergistic combinations.

Hence in view of the content of document D2, the problem to be solved by the present application is the provision of alternative synergistic compositions based on 3-hydroxy-4-aryl-5-oxopyrazoline.

As stated above, the claimed solution represents a selection over the general disclosure of D2. Since that selection does not involve a surprising effect or an advantage over the teaching of document D2, the presently claimed matter does not involve an inventive step (Art. 33(3) PCT).

Re Item VI

Certain published documents (Rule 70.10)

Application No Patent No	Publication date *(day/month/year)*	Filing date *(day/month/year)*	Priority date *(valid claim)* *(day/month/year)*
WO 99 47525 A	23-09-00	11-03-99	13-03-98
D4			08-12-98

Document D4 as published on the 23-09-00 and being filed on the 11-03-99, i.e. before the priority date of the present application (07-09-99) will be part of the prior art under Art. 54(3) EPC relevant to assess novelty when the present application enters the European Regional Phase.

In view of the content of said document, the presently claimed matter seems to be new since document D4 describe compositions containing safeners but does not refer to synergistic effect.

Re Item VII

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document D2 is not mentioned in the description, nor is this document identified therein.

2. In claim 1, concerning the formulation of the groups Z1, Z2 and Z3, it seems that the expressions for example, -C=R6R7-O-CO-C=R8R9...should be replaced by -CR6R7-O-CO-CR8(R9)...

3. Contrary to the assessment on page 12, paragraph 3, the compounds of formula I do not seem to be described on the Pesticide Manual, eleventh edition.

Re Item VIII

1. See point V.A

2. No definition of X6 is given, rendering thereby the claims obscure (Art. 6 PCT).

3. A descrepancy appears between the subject matter of claims 4-7 and their counterpart in the description on page 30, lines 11-21. The description states as (b) herbicide glufosinate, whereas the claims do not define said herbicide, rendering thereby the scope of the claim obscure (Art. 6 PCT).

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
PH/5 -31140A		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP 00/ 08658	05/09/2000	07/09/1999
Applicant		
NOVARTIS AG		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. --

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PC[redacted] 00/08658

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N43/90 A01N25/32 //(A01N43/90,43:76,43:40,35:10,27:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 21652 A (CIBA GEIGY AG ;BOEGER MANFRED (DE); MAIENFISCH PETER (CH); CEDERBA) 18 July 1996 (1996-07-18) cited in the application page 1 -page 2, line 10 page 7, paragraph 3 page 16, last paragraph -page 18, paragraph 1 page 19, last paragraph -page 20, paragraph 1 page 30, paragraph 2 -page 31, paragraph 2 page 72, table 8; page 85, example B8 claims 1,40,57 --- -/--	1-7

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 December 2000	28/12/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Muellners, W

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PC[redacted] 00/08658

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 508 126 A (BAYER AG) 14 October 1992 (1992-10-14) page 3 -page 4, line 21 page 30, line 16 -page 31, line 40 pages 33-40, table 1 claims 1,3,4,11-14	1-7
P,A	WO 99 47525 A (NOVARTIS ERFINDUNGEN VERWALTUN ;MUEHLEBACH MICHEL (CH); GLOCK JUTT) 23 September 1999 (1999-09-23) page 1 -page 2, paragraph 1 page 19, paragraph 2 -page 20, paragraph 2 page 31, table 9; page 33, table 11 page 50, last paragraph -page 54 page 59, example H9; pages 62-67, table 1; pages 86-90, biological examples claims 1,14-18	1-7
A	DE 197 28 568 A (BAYER AG) 22 January 1998 (1998-01-22) page 2 -page 3, line 31 page 4, line 25 - line 32	1-7

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
P[redacted]EP 00/08658

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9621652 A	18-07-1996	AU 4435396 A	31-07-1996
		BR 9600088 A	27-01-1998
		CA 2210286 A	18-07-1996
		CN 1175248 A	04-03-1998
		EP 0804422 A	05-11-1997
		JP 10512248 T	24-11-1998
		TR 960702 A	21-08-1996
		ZA 9600243 A	19-08-1996
EP 0508126 A	14-10-1992	DE 4109208 A	24-09-1992
		BR 9200983 A	17-11-1992
		DE 59208415 D	05-06-1997
		ES 2101764 T	16-07-1997
		GR 3023621 T	29-08-1997
		JP 5117240 A	14-05-1993
		KR 212941 B	02-08-1999
		MX 9201103 A	21-12-1992
		US 5474974 A	12-12-1995
		US 5661110 A	26-08-1997
		US 5739389 A	14-04-1998
		US 5780394 A	14-07-1998
		US 5332720 A	26-07-1994
		US 5358924 A	25-10-1994
WO 9947525 A	23-09-1999	AU 3410999 A	11-10-1999
DE 19728568 A	22-01-1998	CA 2210273 A	17-01-1998
		FR 2751174 A	23-01-1998
		GB 2315413 A,B	04-02-1998
		US 5985797 A	16-11-1999

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 March 2001 (15.03.2001)

PCT

(10) International Publication Number
WO 01/17351 A1

(51) International Patent Classification[7]: A01N 43/90, 25/32 // (A01N 43/90, 43:76, 43:40, 35:10, 27:00)

(21) International Application Number: PCT/EP00/08658

(22) International Filing Date:
5 September 2000 (05.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1641/99 7 September 1999 (07.09.1999) CH

(71) Applicant *(for all designated States except US)*: SYNGENTA PARTICIPATIONS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: GLOCK, Jutta [DE/CH]; Rifeldweg 6, CH-4322 Mumpf (CH). FRIEDMANN, Adrian, Alberto [CH/CH]; Hebelstrasse 95, CH-4056 Basel (CH). CORNES, Derek [GB/CH]; Bettenstrasse 22, CH-4123 Allschwil (CH).

(74) Agent: SYNGENTA PARTICIPATIONS AG; Intellectual Property, P.O. Box, CH-4002 Basel (CH).

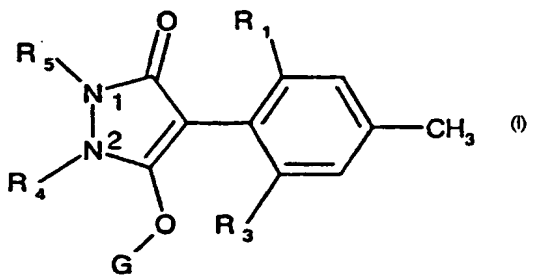
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HERBICIDAL COMPOSITION



(I)

(57) Abstract: A selective herbicidal composition for controlling grasses and weeds in crops of cultivated plants, comprising: a) a herbicidally effective amount of a compound of formula (I), wherein the substituents are defined as given in claim (1); b) a herbicidally synergistic amount of at least one herbicide selected from the classes of phenoxy-phenoxypropionic acids, hydroxylamines, sulfonylureas, imidazolinones, pyrimidines, triazines, ureas, PPO, chloroacetanilides, phenoxyacetic acids, triazinones, dinitroanilines, azinones, carbamates, oxyacetamides, thiolcarbamates, azole-ureas, benzoic acids, anilides, nitriles, triones and sulfonamides, as well as from the herbicides amitrol, benfuresate, bentazone, cinmethylin, clomazone, chlopyralid, difenzoquat, dithiopyr, ethofumesate, flurochloridone, indanofane, isoxaben, oxaziclomefone, pyridate, pyridafol, quinchlorac, quinmerac, tridiphane and flamprop; and optionally c) to antagonise the herbicide, and antidotally effective amount of a safener selected from cloquintocet, an alkali, alkaline earth, sulfonium or ammonium cation of cloquintocet, cloquintocet-mexyl, mefenpyr, an alkali, alkaline earth, sulfonium or ammonium cation of mefenpyr and mefenpyr-diethyl; and/or d) an additive comprising an oil of vegetable or animal origin, a mineral oil, the alkylesters thereof or mixtures of these oils and oil derivatives.

WO 01/17351 A1

Herbicidal composition

The present invention relates to novel selective herbicidal synergistic compositions for controlling grasses and weeds in crops of cultivated plants, especially in crops of maize and cereals, which comprise a 3-hydroxy-4-(4-methylphenyl)-5-oxo-pyrazoline herbicides, a synergistically active amount of at least one second herbicide, as well as optionally an oil additive and/or a safener (antidote), and to the use of said compositions for controlling weeds in crops of cultivated plants.

When applying herbicides, the cultivated plants may also suffer severe damage owing to factors that include the concentration of the herbicide and the mode of application, the cultivated plant itself, the nature of the soil, and the climatic conditions such as exposure to light, temperature and rainfall. To counteract this problem and similar ones, the proposal has already been made to use different compounds as safeners which are able to antagonise the harmful action of the herbicide on the cultivated plant, i.e. to protect the cultivated plant while leaving the herbicidal action on the weeds to be controlled virtually unimpaired.

It has, however, been found that the proposed safeners often have a very specific action with respect not only to the cultivated plants but also to the herbicide, and in some cases also subject to the mode of application, i.e. a specific safener will often be suitable only for a specific cultivated plant and a specific class of herbicide or a specific herbicide. For example, it has been found that the safeners cloquintocet or cloquintocet-mexyl and mefenpyr or mefenpyr-diethyl, which are known from EP-A-0 191 736 (comp. 1.316) and WO 91/07874 (example 3) as well as from The Pesticide Manual, 11ed. , British Crop Protection Council, Entry Nos. 154 and 462, can indeed protect the cultivated plants from the phytotoxic action of in particular 3-hydroxy-4-(4-methylphenyl)-5-oxo-pyrazoline derivatives, but partly attenuate the herbicidal action on weeds.

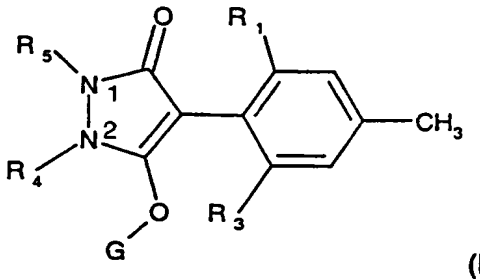
It is known from US-A-4,834,908 that certain combinations of oil additives can increase the herbicidal action of compounds from the class of cyclohexanediones, benzothiadiazinone dioxides, diphenylether herbicides and aryloxyphenoxy herbicides.

Although the 3-hydroxy-4-(4-methylphenyl)-5-oxo-pyrazoline derivatives are structurally completely different from the compounds disclosed in US-A-4,834,908, the combination of oil additives of this kind with these 3-hydroxy-4-(4-methylphenyl)-5-oxo-pyrazoline derivatives likewise leads to an increase in herbicidal action, but the cultivated plant is also harmed to a considerable extent. Therefore, this herbicide/oil additive mixture is not suitable for the selective control of weeds in crops of cultivated plants.

It has now surprisingly been found that, when using these special 3-hydroxy-4-(4-methylphenyl)-5-oxo-pyrazoline herbicides, weeds can be selectively controlled with great success without harming the cultivated plant, by applying these compounds in combination with a herbicidally synergistic amount of at least one second herbicide, and optionally also with an additive comprising an oil of vegetable or animal origin or a mineral oil, or the alkylesters thereof or mixtures of these oils and oil derivatives, and/or with the safeners cloquintocet or mefenpyr.

The object of the present invention is thus a selective herbicidal composition comprising, in addition to customary inert formulation assistants such as carriers, solvents and wetting agents, as the active ingredient, a mixture of

a) a herbicidally effective amount of a compound of formula I



(I),

wherein

R_1 and R_3 independently of one another are halogen, nitro, cyano, C_1-C_4-alkyl, C_2-C_4-alkenyl, C_2-C_4-alkinyl, C_1-C_4-halogenalkyl, C_2-C_6-halogenalkenyl, C_3-C_6-cycloalkyl, halogen-substituted C_3-C_6-cycloalkyl, C_2-C_6-alkoxyalkyl, C_2-C_6-alkylthioalkyl, hydroxy, mercapto, C_1-C_6-alkoxy, C_3-C_6-alkenyloxy, C_3-C_6-alkinyloxy, carbonyl, carboxyl, C_1-C_4-alkylcarbonyl, C_1-C_4-hydroxyalkyl, C_1-C_4-alkoxycarbonyl, C_1-C_4-alkylthio, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, amino, C_1-C_4-alkylamino or di-(C_1-C_4-alkyl)-amino;

R_4 and R_5 together signify a group

$$-C\text{-}R_6(R_7)\text{-}O\text{-}C\text{-}R_8(R_9)\text{-}C\text{-}R_{10}(R_{11})\text{-}C\text{-}R_{12}(R_{13})- \quad (Z_1),$$

-C-R_{14}(R_{15})-C-R_{16}(R_{17})-O-C-R_{18}(R_{19})-C-R_{20}(R_{21})- (Z_2), or

-C-R_{22}(R_{23})-C-R_{24}(R_{25})-C-R_{26}(R_{27})-O-C-R_{28}(R_{29})-; (Z_3) ;

wherein R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, R_{26}, R_{27}, R_{28}, and R_{29} independently of one another are hydrogen, halogen, C_1-C_4-alkyl or C_1-C_4-halogenalkyl, whereby an alkylene ring, which together with the carbon atoms of groups Z_1, Z_2 or Z_3 contains 2 to 6 carbon atoms and may be interrupted by oxygen, may be either anellated or spiro-linked to the carbon atoms of groups Z_1, Z_2 or Z_3, or this alkylene ring overbridges at least one ring atom of groups Gruppen Z_1, Z_2 or Z_3 ;

G is hydrogen, -C(X_1)-R_{30}, -C(X_2)-X_3-R_{31}, -C(X_4)-N(R_{32})-R_{33}, -SO_2-R_{34}, an alkaline, alkaline earth, sulfonium or ammonium cation or -P(X_5)(R_{35})-R_{36} or -CH_2-X_6-R_{37} ;

X_1, X_2, X_3, X_4, X_5 and X_5 independently of one another, are oxygen or sulfur;

R_{30}, R_{31}, R_{32} and R_{33} independently of one another, are hydrogen, C_1-C_{10}-alkyl, C_1-C_{10}-halogenalkyl, C_1- C_{10}-cyanoalkyl, C_1- C_{10}-nitroalkyl, C_1- C_{10}-aminoalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7-cyclalkyl-C_1-C_5-alkyl, C_2- C_{10}-alkoxy-alkyl, C_4-C_{10}-alkenyloxy-alkyl, C_4- C_{10}-alkinyloxy-alkyl, C_2- C_{10}-alkylthio-alkyl, C_1-C_5-alkysulfoxyl- C_1-C_5-alkyl, C_1-C_5-alkylsulfonyl-C_1-C_5-alkyl, C_2-C_8-alkylideneamino-oxy-C_1-C_5-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_5-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_5-alkyl, C_1-C_5-amino-carbonyl-C_1-C_5-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_5-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_5-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_5-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl- C_1-C_5-alkyl, heteroaryl- C_1-C_5-alkyl, phenoxy- C_1-C_5-alkyl, heteroaryloxy- C_1-C_5-alkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, phenyl; or phenyl substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or heteroaryl or heteroarylamino; heteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diheteroarylamino, diheteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; phenylamino, phenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diphenylamino, diphenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkylamino, C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; di-C_3-C_7-cycloalkylamino, di-C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkoxy or C_3-C_7-cycloalkoxy substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro;

R_{34}, R_{35} and R_{36} independently of one another, are hydrogen, C_1-C_{10}-alkyl, C_1-C_{10}-halogenalkyl, C_1- C_{10}-cyanoalkyl, C_1- C_{10}-nitroalkyl, C_1- C_{10}-aminoalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7-cyclalkyl-C_1-C_5-alkyl, C_2- C_{10}-alkoxy-alkyl, C_4-C_{10}-alkenyloxy-alkyl, C_4- C_{10}-alkinyloxy-alkyl, C_2- C_{10}-alkylthio-alkyl, C_1-C_5-alkysulfoxyl- C_1-C_5-alkyl, C_1-C_5-alkylsulfonyl-C_1-C_5-alkyl, C_2-C_8-alkylideneamino-oxy-C_1-C_5-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_5-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_5-alkyl, C_1-C_5-amino-carbonyl-C_1-C_5-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_5-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_5-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_5-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl- C_1-C_5-alkyl, heteroaryl- C_1-C_5-alkyl, phenoxy- C_1-C_5-alkyl, heteroaryloxy- C_1-C_5-alkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, phenyl; or phenyl substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or heteroaryl or heteroarylamino; heteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diheteroarylamino, diheteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; phenylamino, phenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diphenylamino, diphenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkylamino, C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; di-C_3-C_7-cycloalkylamino, di-C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkoxy or C_3-C_7-cycloalkoxy substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_1-C_{10}-alkoxy, C_1-C_{10}-halogenalkoxy, C_1-C_5-alkylamino, C_2-C_8-dialkylamino as well as benzyloxy or phenoxy, whereby the benzyl and phenyl groups in turn may be substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano, formyl, acetyl, propionyl, carboxyl, C_1-C_5-alkoxycarbonyl, methylthio, ethylthio, or nitro;

and

R_{37} is C_1-C_{10}-alkyl, C_1-C_{10}-halogenalkyl, C_1- C_{10}-cyanoalkyl, C_1- C_{10}-nitroalkyl, C_1- C_{10}-aminoalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7-cyclalkyl-C_1-C_5-alkyl, C_2- C_{10}-alkoxy-alkyl, C_4- C_{10}-alkenyloxy-alkyl, C_4- C_{10}-alkinyloxy-alkyl, C_2- C_{10}-alkylthio-alkyl, C_1-C_5-alkysulfoxyl- C_1-C_5-alkyl, C_1-C_5-alkylsulfonyl-C_1-C_5-alkyl, C_2-C_8-alkylideneamino-oxy-C_1-C_5-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_5-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_5-alkyl, C_1-C_5-amino-carbonyl-C_1-C_5-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_5-alkyl, C_1-C_5-

alkylcarbonylamino-C_1-C_5-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_5-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl- C_1-C_5-alkyl, heteroaryl- C_1-C_5-alkyl, phenoxy- C_1-C_5-alkyl, heteroaryloxy- C_1-C_5-alkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, phenyl; or phenyl substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or heteroaryl or heteroarylamino; heteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diheteroarylamino, diheteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; phenylamino, phenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diphenylamino, diphenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkylamino, C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; di-C_3-C_7-cycloalkylamino, di-C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkoxy or C_3-C_7-cycloalkoxy substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or C_1-C_{10}-alkylcarbonyl; as well as salts and diastereoisomers of the compounds of formula I, with the proviso that R_1 and R_3 are not simultaneously methyl; and;

b) a herbicidally synergistic amount of at least one herbicide selected from the classes of phenoxy-phenoxypropionic acids, hydroxylamines, sulfonylureas, imidazolinones, pyrimidines, triazines, ureas, PPO, chloroacetanilides, phenoxyacetic acids, triazinones, dinitroanilines, azinones, carbamates, oxyacetamides, thiolcarbamates, azole-ureas, benzoic acids, anilides, nitriles, triones and sulfonamides, as well as from the herbicides amitrol, benfuresate, bentazone, cinmethylin, clomazone, chlopyralid, difenzoquat, dithiopyr, ethofumesate, flurochloridone, indanofane, isoxaben, oxaziclomefone, pyridate, pyridafol, quinchlorac, quinmerac, tridiphane and flamprop; and optionally

c) to antagonise the herbicide, an antidotally effective amount of a safener selected from cloquintocet, an alkali, alkaline earth, sulfonium or ammonium cation of cloquintocet, cloquintocet-mexyl, mefenpyr, an alkali, alkaline earth, sulfonium or ammonium cation of mefenpyr and mefenpyr-diethyl; and/or

d) an additive comprising an oil of vegetable or animal origin, a mineral oil, the alkylesters thereof or mixtures of these oils and oil derivatives.

In the above definitions, halogen is understood to mean fluorine, chlorine, bromine and iodine, preferably fluorine, chlorine and bromine. The alkyl groups occurring in the definitions of the substituents may be for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl or tert-butyl, as well as the pentyl and hexyl isomers. Appropriate cycloalkyl substituents contain 3 to 6 carbon atoms and are, for example, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. They may be mono- or polysubstituted by halogen, preferably fluorine, chlorine or bromine. Alkenyl is understood to be for example vinyl, allyl, methallyl, 1-methylvinyl or but-2-en-1-yl Alkinyl signifies for example ethinyl, propargyl, but-2-in-1-yl, 2-methylbutin-2-yl or but-3-in-2-yl. Halogenalkyl groups preferably have a chain length of 1 to 4 carbon atoms. Halogenalkyl is for example fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1.1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl and 2,2,2-trichloroethyl; preferably trichloromethyl, difluorochloromethyl, difluoromethyl, trifluoromethyl and dichlorofluoromethyl. Halogenalkenyl may be alkenyl groups that are mono- or polysubstituted by halogen, halogen signifying fluorine, chlorine, bromine and iodine, especially fluorine and chlorine, for example 2,2-difluoro-1-methylvinyl, 3-fluoropropenyl, 3-chloropropenyl, 3-bromopropenyl, 2,3,3-trifluoropropenyl, 2,3,3-trichloropropenyl and 4,4,4-trifluoro-but-2-en-1-yl. Of the C_2-C_6-alkenyl groups mono-, di- or trisubstituted by halogen, preference is given to those having a chain length of 3 to 5 carbon atoms. Alkoxy groups preferably have a chain length of 1 to 6 carbon atoms. Alkoxy is for example methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec.-butoxy and tert.-butoxy, as well as the isomers pentyloxy and hexyloxy, preferably methoxy and ethoxy. Alkoxycarbonyl is preferably acetyl or propionyl. Alkoxycarbonyl signifies for example methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, iso-propoxycarbonyl, n-butoxycarbonyl, iso-butoxycarbonyl, sec.-butoxycarbonyl or tert.-butoxycarbonyl; preferably methoxycarbonyl or ethoxycarbonyl. Alkylthio groups preferably have a chain length of 1 to 4 carbon atoms. Alkylthio is for example methylthio, ethylthio, propylthio, iso-propylthio, n-butylthio, iso-butylthio, sec.-butylthio or tert.-butylthio, preferably methylthio and ethylthio. Alkylsulfinyl is for example methylsulfinyl, ethylsulfinyl, propylsulfinyl, iso-propylsulfinyl, n-butylsulfinyl, iso-butylsulfinyl, sec.-butylsulfinyl, tert.-butylsulfinyl; preferably methylsulfinyl and ethylsulfinyl. Alkylsulfonyl is for example methylsulfonyl, ethylsulfonyl, propylsulfonyl,

iso-propylsulfonyl, n-butylsulfonyl, iso-butylsulfonyl, sec.-butylsulfonyl or tert.-butylsulfonyl; preferably methylsulfonyl or ethylsulfonyl. Alkylamino is for example methylamino, ethylamino, n-propylamino, isopropylamino or the isomeric butylamines. Dialkylamino is for example dimethylamino, methylethylamino, diethylamino, n-propylmethylamino, dibutylamino and di-isopropylamino. Alkoxyalkyl groups preferably have 2 to 6 carbon atoms. Alkoxyalkyl signifies for example methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl or isopropoxyethyl. Alkylthioalkyl signifies for example methylthiomethyl, methylthioethyl, ethylthiomethyl, ethylthioethyl, n-propylthiomethyl, n-propylthioethyl, isopropylthiomethyl, isopropylthioethyl, butylthiomethyl, butylthioethyl or butylthiobutyl. Phenyl may be present in substituted form. In this case, the substituents may be in ortho-, meta- and/or para-position. Preferred substituent positions are the ortho- and para-positions to the ring connection point.

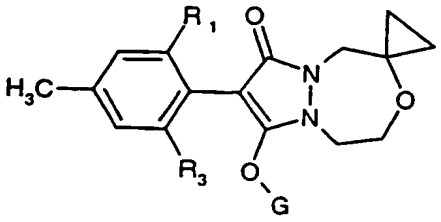
Heteroaryl groups are usually aromatic heterocycles, which contain preferably 1 to 3 hetero atoms selected from nitrogen, oxygen and sulfur. Examples of suitable heterocycles and heteroaromatics are: pyrrolidine, piperidine, pyran, dioxane, azetidine, oxetane, pyridine, pyrimidine, triazine, thiazole, thiadiazole, imidazole oxazole, isoxazole as well as pyrazine, furan, morpholine, piperazine, pyrazole, benzoxazole, benzothiazole, quinoxaline and quinoline. These heterocycles and heteroaromatics may be further substituted, for example by halogen, alkyl, alkoxy, haloalkyl, haloalkoxy, nitro, cyano, thialkyl, alkylamino or phenyl.

The C_2-C_{10}-alkenyl- and alkinylgruppen R_{34} may be mono- or polyunsaturated. They preferably contain 2 to 12, especially 2 to 6 carbon atoms.

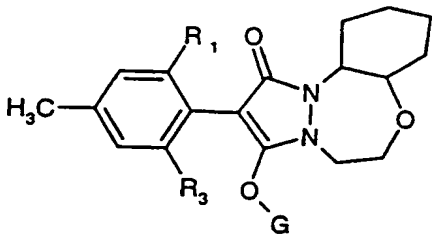
Alkali, alkaline earth or ammonium cations for the substituents G are for example the cations of sodium, potassium, magnesium, calcium and ammonium. Preferred sulfonium cations are especially trialkylsulfonium cations, in which the alkyl radicals preferably each contain 1 to 4 carbon atoms.

The left free valency of groups Z_1, Z_2 and Z_3 is bonded at position 1 and the right free valency is bonded at position 2 of the pyrazoline ring.

Compounds of formula I, in which an alkylene ring may be anellated or spiro-linked to groups Z_1, Z_2 and Z_3, giving 2 to 6 carbon atoms together with the carbon atoms of groups Z_1, Z_2 and Z_3, have for xample the following structure:

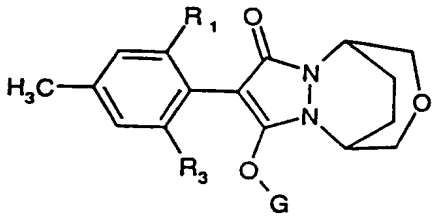


(spiro-linked) or



(anellated).

Compounds of formula I, in which an alkylene ring in groups Z_1, Z_2 or Z_3 overbridges at least one ring atom of groups Z_1, Z_2 or Z_3 , have for example the following structure:



(overbridged).

Preferred herbicides of formula I for the composition according to the invention are characterised in that R_1 and R_3, independently of one another, signify ethyl, halogenethyl, ethinyl, C_1-C_2-alkoxy or C_1-C_2-halogenalkoxy.

Also preferred are those compositions according to the invention in which R_4 and R_5 together form a group Z_2 -C-R_{14}(R_{15})-C-R_{16}(R_{17})-O-C-R_{18}(R_{19})-C-R_{20}(R_{21})- (Z_2) , wherein R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21} most preferably signify hydrogen.

A further preferred group of compositions according to the invention is characterised in that R_{30}, R_{31}, R_{32} and R_{33} independently of each other, signify hydrogen, C_1-C_8-alkyl, C_1-C_8-halogenalkyl, C_1- C_8-cyanoalkyl, C_1- C_8-nitroalkyl, C_1- C_8-aminoalkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7.cycloalkyl-C_1-C_5-alkyl, C_2-C_4-alkoxy-alkyl, C_4-C_6-alkenyloxy-alkyl, C_4-C_6-alkinyloxy-alkyl, C_2-C_4-alkylthio-alkyl, C_1-C_4-alkysulfinyl-C_1-C_2-alkyl, C_1-C_2-alkylsulfonyl-C_1-C_2-alkyl, C_2-C_4-alkylideneamino-oxy-C_1-C_2-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_2-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_2-alkyl, C_1-C_5-amino-carbonyl-C_1-C_2-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_2-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_2-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_2-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl-C_1-C_2-alkyl, heteroaryl- C_1-C_2-alkyl, phenoxy-C_1-C_2-alkyl, heteroaryloxy-C_1-C_2-alkyl, phenyl or heteroaryl;
R_{34}, R_{35} and R_{36} independently of each other, signify hydrogen, C_1-C_8-alkyl, C_1-C_8-halogenalkyl, C_1- C_8-cyanoalkyl, C_1- C_8-nitroalkyl, C_1- C_8-aminoalkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7.cycloalkyl-C_1-C_5-alkyl, C_2-C_4-alkoxy-alkyl, C_4-C_6-alkenyloxy-alkyl, C_4-C_6-alkinyloxy-alkyl, C_2-C_4-alkylthio-alkyl, C_1-C_4-alkysulfinyl-C_1-C_2-alkyl, C_1-C_2-alkylsulfonyl-C_1-C_2-alkyl, C_2-C_4-alkylideneamino-oxy-C_1-C_2-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_2-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_2-alkyl, C_1-C_5-amino-carbonyl-C_1-C_2-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_2-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_2-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_2-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl-C_1-C_2-alkyl, heteroaryl- C_1-C_2-alkyl, phenoxy-C_1-C_2-alkyl, heteroaryloxy-C_1-C_2-alkyl, phenyl or heteroaryl, benzyloxy or phenoxy, whereby the benzyl and phenyl groups in turn may be substituted by halogen, nitro, cyano, amino, dimethylamino, hydroxy, methoxy, ethoxy, methylthio, ethylthio, formyl, acetyl, propionyl, carboxyl, C_1-C_5-alkoxycarbonyl or C_1- or C_2-halogenalkyl; and
R_{37} signifies C_1-C_8-alkyl, C_1-C_8-halogenalkyl, C_1- C_8-cyanoalkyl, C_1- C_8-nitroalkyl, C_1- C_8-aminoalkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7.cycloalkyl-C_1-C_5-alkyl, C_2-C_4-alkoxy-alkyl, C_4-C_6-alkenyloxy-alkyl, C_4-C_6-alkinyloxy-alkyl, C_2-C_4-alkylthio-alkyl, C_1-C_4-alkysulfinyl-C_1-C_2-alkyl, C_1-C_2-alkylsulfonyl-C_1-C_2-alkyl, C_2-C_4-alkylideneamino-oxy-C_1-C_2-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_2-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_2-alkyl, C_1-C_5-amino-carbonyl-C_1-C_2-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_2-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_2-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_2-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl-C_1-C_2-alkyl, heteroaryl- C_1-C_2-alkyl, phenoxy-C_1-C_2-alkyl, heteroaryloxy-C_1-C_2-alkyl, phenyl or heteroaryl,

benzyloxy or phenoxy, whereby the benzyl and phenyl groups in turn may be substituted by halogen, nitro, cyano, amino, dimethylamino, hydroxy, methoxy, ethoxy, methylthio, ethylthio, formyl, acetyl, propionyl, carboxyl, C_1-C_2-alkoxycarbonyl or C_1- or C_2-halogenalkyl; or R_{37} signifies C_1-C_8-alkylcarbonyl.

Especially preferred are those compositions according to the invention in which, in formula I, R_{30}, R_{31}, R_{32} and R_{33} , independently of each other, signify hydrogen, C_1-C_8-alkyl, C_1-C_8-halogenalkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl,C_3-C_8-cycloalkyl, C_3-C_7-cycloalkyl-C_1-C_2-alkyl, C_2-C_4-alkoxy-alkyl, phenyl, heteroaryl, phenyl-C_1-C_2-alkyl, heteroaryl-C_1-C_2-alkyl, phenoxy-C_1-C_2-alkyl, heteroaryloxy-C_1-C_2-alkyl;
R_{34}, R_{35} and R_{36} independently of each other, signify hydrogen, C_1-C_8-alkyl, C_1-C_8-halogenalkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, C_3-C_7-cycloalkyl-C_1-C_2-alkyl, C_2-C_4-alkoxy-alkyl, phenyl, heteroaryl, phenyl-C_1-C_2-alkyl, heteroaryl- C_1-C_2-alkyl, phenoxy-C_1-C_2-alkyl, heteroaryloxy-C_1-C_2-alkyl, C_1-C_6-alkoxy, C_1-C_3-alkylamino or di-(C_1-C_3-alkyl)-amino; and
R_{37} signifies C_1-C_8-alkyl, C_1-C_8-halogenalkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, C_3-C_7-cycloalkyl-C_1-C_2-alkyl, C_2-C_4-alkoxy-alkyl, phenyl, heteroaryl, phenyl-C_1-C_2-alkyl, heteroaryl- C_1-C_2-alkyl, phenoxy-C_1-C_2-alkyl, heteroaryloxy-C_1-C_2-alkyl, C_1-C_6-alkoxy, C_1-C_3-alkylamino, di-(C_1-C_3-alkyl)-amino or C_1-C_8-alkylcarbonyl.

Of the compositions according to the invention, particular preference is also given to those which contain as the herbicidally effective component a mixture of a compound of formula I and a synergistically effective amount of at least one herbicide selected from diclofop-methyl, fluazifop-P-butyl- quizalafop-P-ethyl, propaquizafop, clodinafop-P-propargyl, cyhalfop-butyl, fenoxaprop-P-ethyl, haloxyfop-methyl, haloxyfop-etoethyl, sethoxidim, alloxydim, clethodim, clefoxydim, cycloxydim, tepralkoxydim, tralkoxydim butroxidim, amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, cinosulfuron, chlorsulfuron, chlorimuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron, fluazasulfuron, flupyrsulfuron, imazosulfuron, iodosulfuron (CAS RN 144550-36-7 and 185119-76-0), metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron, pyrazosulfuron-ethyl, sulfosulfuron, rimsulfuron, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, triflusulfuron-methyl, prosulfuron, flucarbazon, tritosulfuron CAS RN 142469-14-5, imazethapyr, imazamethabenz, imazamethapyr, imazaquin,

imazamox, imazapyr, pyrithiobac-sodium, pyriminobac, bispyribac-sodium, atrazin, butracil, simazin, simethryne, terbutryne, terbuthylazine, trimexyflam, isoproturon, chlortoluron, diuron, dymron, fluometuron, linuron, methabenzthiazuron, glyphosate, sulfosate, glufosinate, nitrofen, bifenox, acifluorfen, lactofen, oxyfluorfen, ethoxyfen, fluoroglycofen, fomesafen, halosafen, azafenidin (CAS RN. - 68049-83-2), benzfendizone (CAS RN 158755-95-4), butafenacil (CAS RN 158755-95-4), carfentrazone-ethyl, cinidon-ethyl (CAS RN 142891-20-1), flumichlorac-pentyl, flumioxazin, fluthiacet-methyl, oxadiargyl (CAS RN 39807-15-3), oxadiazon, pentoxazon (CAS RN 110956-75-7), sulfentrazone, fluazolate (CAS RN 174514-07-9), pyraflufen-ethyl, alachlor, acetochlor, butachlor, dimethachlor, dimethenamid, S-dimethenamid, metazachlor, metolachlor, S-metolachlor, pretilachlor, propachlor, propisochlor, thenylchlor, pethoamid (CAS RN 106700-29-2), 2,4-D, fluroxypyr, MCPA, MCPP, MCPB, trichlorpyr, mecropop-P, hexazinon, metamitron, metribuzin, oryzalin, pendimethalin, trifluralin, chloridazon, norflurazon, chlorpropham, desmedipham, phenmedipham, propham, mefenacet, fluthiacet, butylate, cycloate, diallate, EPTC, esprocarb, molinate, prosulfocarb, thiobencarb, triallate, fentrazamide (CAS RN158237-07-1), cafenstrole, dicamba, picloram, diflufenican, propanil, bromoxynil, dichlobenil, ioxynil, sulcotrione, mesotrione (CAS RN 104206-82-8), isoxaflutole, isoxachlortole (CAS RN 141112-06-3), flucarbazone (CAS RN 181274-17-9), propoxycarbazone (CAS RN 145026-81-9 and 181274-15-7 (sodium salt)), foramsulfuron CAS RN 173159-57-4, penoxsulam (CAS RN 219714-96-2), trifloxysulfuron (CAS RN 145099-21-4 and 199119-58-9 (sodium salt)),

pyriftalid (CAS RN 135186-78-6), trifloxysulfuron CAS RN 145099-21-4 and 199119-58-9 (sodium salt)), pyriftalid (CAS RN 135186-78-6), flufenpyr-ethyl (CAS RN 188489-07-8), profluazol (CAS RN 190314-43-3), pyraclonil (CAS RN 158353-15-2), benfluamid (CAS RN 113604-08-7), picolinafen (CAS RN 137641-05-5), amicarbazone (CAS RN 129909-90-6), flufenpyr-ethyl (CAS RN 188489-07-8), profluazol (CAS RN 190314-43-3), pyraclonil (CAS RN 158353-15-2), benfluamid (CAS RN 113604-08-7), picolinafen (CAS RN 137641-05-5), amicarbazone (CAS RN 129909-90-6), chlorasulam, diclosulam (CAS RN 145701-21-9), florasulam, flumetsulam, metosulam, amitrol, benfuresate, bentazone, cinmethylin, clomazone, chlopyralid, difenzoquat, dithiopyr, ethofumesate, flurochloridone, indanofane, isoxaben, oxaziclomefone (CAS RN 153197-14-9), pyridate, pyridafol (CAS RN 40020-01-7), quinchlorac, quinmerac, tridiphane and flamprop. The abbreviation CAS RN indicates the registration number in Chemical Abstracts.

The compositions according to the invention preferably contain
a) a herbicide of formula I in combination with:
b) a herbicidally synergistic amount of a second herbicide according to the invention,
c) a safener and
d) an oil additive.

Of the synergistically active herbicides b), those of the class of sulfonylureas and phenoxy-phenoxypropionic acids are preferred, with particular preference being given for example to clodinafop-propargyl known from The Pesticide Manual, 11th ed. , British Crop Protection Council, Entry No. 147 and triasulfurone known from The Pesticide Manual, 11th ed. , British Crop Protection Council, Entry No. 723. An especially preferred safener c) is cloquintocet-mexyl. In terms of the present invention, MERGE® and Actiprom® are especially notable as suitable oil additives.

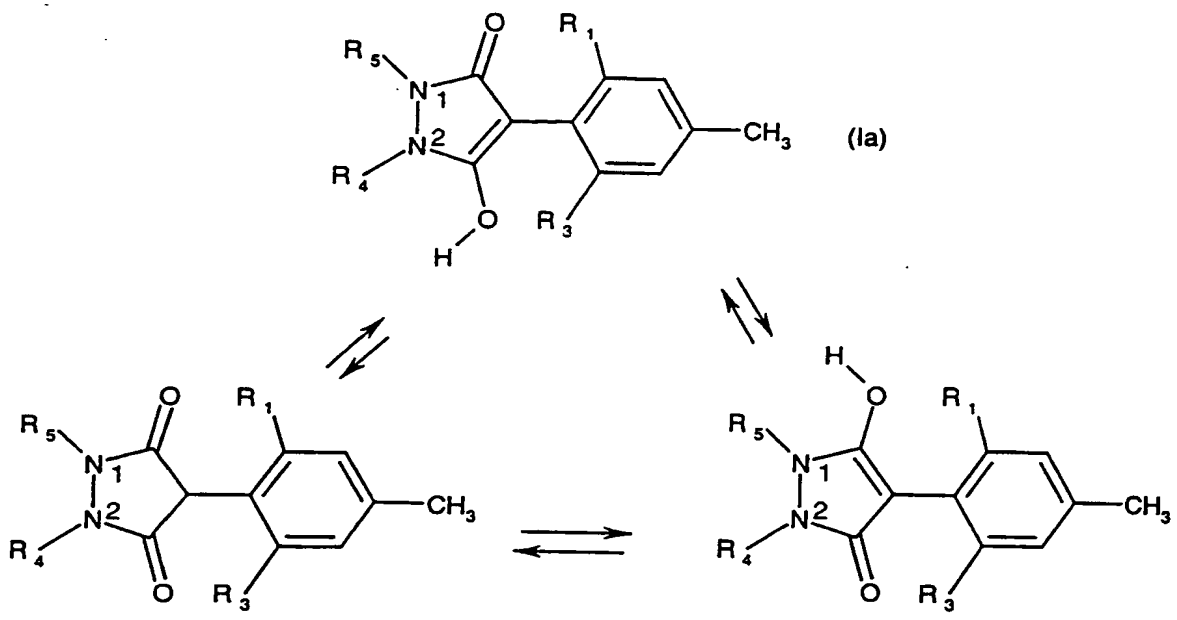
If not otherwise stated, the above-mentioned components of the compound of formula I are known from The Pesticide Manual, Eleventh Edition, 1997, BCPC. The components of the compound of formula I may, if desired, also be present in the form of esters or salts, as named e.g. in The Pesticide Manual, Eleventh Edition, 1997, BCPC. Butafenacil is known from US-A-5.183.492. Pethoamid has the CAS registration number 106700-29-2. Mesotrione is known from US-A-5,006,158.

The compositions according to the invention may also contain salts which the compounds of formula I can form with acids. Suitable acids for the formation of the acid addition salts are both organic and inorganic acids. Examples of such acids are hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acids, sulfuric acid, acetic acid, propionic acid, butyric acid, valeric acid, oxalic acid, malonic acid, fumaric acid, organic sulfonic acids, lactic acid, tartaric acid, citric acid and salicylic acid. The salts of compounds of formula I with acidic hydrogen are also alkali metal salts, e.g. sodium and potassium salts; alkaline earth metal salts, e.g. calcium and magnesium salts; ammonium salts, i.e. unsubstituted ammonium salts and mono- or polysubstituted ammonium salts, as well as salts with other organic nitrogen bases. Corresponding salt-forming components are alkali and alkaline earth metal hydroxides, especially the hydroxides of lithium, sodium, potassium, magnesium or calcium, with special significance being given to those of sodium or potassium.

Illustrative examples of amines suitable for forming ammonium salts are ammonia, as well as primary, secondary, and tertiary C_1-C_{18}-alkylamines, C_1-C_4-hydroxyalkylamines and C_2-C_4-alkoxyalkylamines, typically methylamine, ethylamine, n-propylamine, isopropylamine, the four isomeric butylamines, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methyl ethylamine, methyl isopropylamine, methyl hexylamine, methyl nonylamine, methyl pentadecylamine, methyl octadecylamine, ethyl butylamine, ethyl heptylamine, ethyl octylamine, hexyl heptylamine, hexyl octylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, isopropanolamine, N,N-diethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl--2-amine, dibutenyl-2-amine, n-hexenyl-2-amine, propylenediamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-sec-butylamine, tri-n-amylamine, methoxyethylamine and ethoxyethylamine; heterocyclic amines such as pyridine, quinoline, isoquinoline, morpholine, N-methylmorpholine, thiomorpholine, piperidine, pyrrolidine, indoline, quinuclidine and azepine; primary arylamines such as anilines, methoxyanilines, ethoxyanilines, o-, m- and p-toluidines, phenylendiamines, benzidines, naphthylamines and o-, m- and p-chloroanilines. Preferred amines are triethylamine, isopropylamine and diisopropylamine.

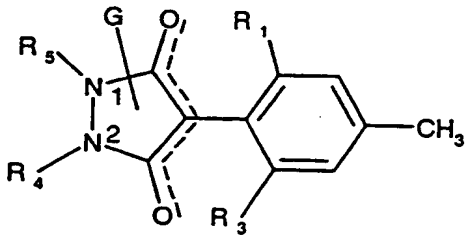
In the methods described in this application, if non-chiral educts are used, the unsymmetrically substituted compounds of formula I generally occur as racemates. The stereoisomers may then be separated by known methods, such as fractional crystallisation following salt formation with optically pure bases, acids or metal complexes, or by chromatographic methods, e.g. high pressure liquid chromatography (HPLC) on acetyl cellulose, on the basis of physical-chemical properties. In the present invention, the compounds of formula I are understood to include both the concentrated and optically pure forms of each stereoisomer, and the racemates or diastereoisomers. If there is no specific reference to the individual optical antipodes, the racemic mixtures under the given formula are understood to be those which are obtained in the indicated preparation process. If there is an aliphatic C=C-double bond, then geometric isomerism may also occur.

Depending on the type of substituents, the compounds of formula I may also exist as geometric and/or optical isomers and isomer mixtures, and as tautomers and tautomer mixtures. For example, the compounds of formula I, in which the group G signifies hydrogen, may exist in the following tautomeric equilibria.



(Ia) (Ib) (Ic)

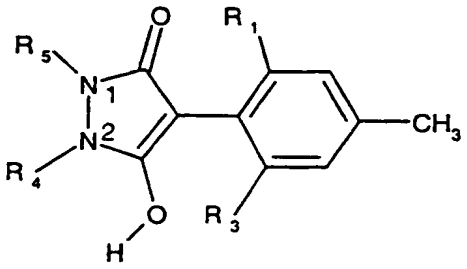
If G is other than hydrogen and Z signifies the group Z_1 or Z_3, or if G is other than hydrogen and Z_2 is unsymmetrically substituted, anellated or spiro-linked, the compound of formula I may exist as the isomer of formula Id



(Id)

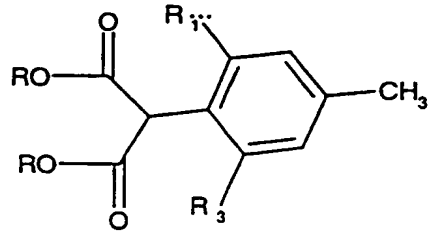
Methods of preparing compounds, which are different in respect of the significance of substituents R_4 and R_5 from the compounds of formula I of the present invention, are described for example in WO 96/21652. The compounds of formula I of the present invention may be prepared in analogous manner to the methods described in WO 96/21652.

The compounds of formula II used as starting products for such methods



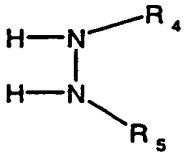
(II)

wherein R_1, R_3, R_4 and R_5 are defined as given in formula I, may be prepared for example whereby a compound of formula III

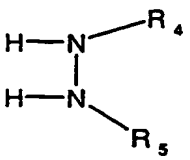


(III),

in which R is C_1-C_6-alkyl, C_1-C_6-halogenalkyl, preferably methyl, ethyl or trichloroethyl, and R_1 and R_3 are defined as given in formula I, is reacted in an inert organic solvent, optionally in the presence of a base, with a compound of formula IV or IVa



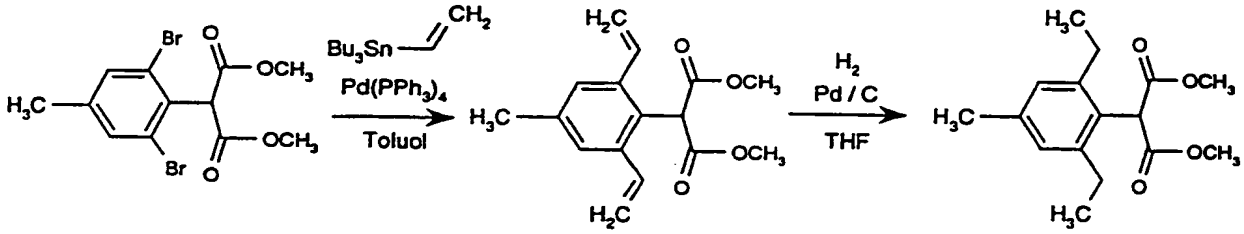
• 2HBr (IV),



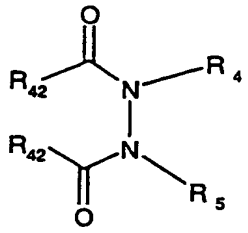
(IVa),

wherein R_4 and R_5 are defined as in formula I. Further preparation methods for compounds of formula II are also described for example in WO 92/16510.

The compounds of formula III are either known or may be produced analogously to known methods. Methods for the preparation of compounds of formula III, as well as the reaction thereof with hydrazines, are described for example in WO 97/02243. Compounds of formula III, wherein R is C_1-C_6-alkyl, C_1-C_6-halogenalkyl, preferably methyl, ethyl or trichloroethyl, and R_1, R_2 and R_3 are defined as given in formula I, may be prepared by methods known to those skilled in the art. For example, compounds of formula III, wherein R is C_1-C_6-alkyl, C_1-C_6-halogenalkyl, preferably methyl, ethyl or trichloroethyl, and R_1, R_2 and R_3 , independently of each other, are C_1-C_4-alkyl, C_2-C_4-alkenyl, C_2-C_4-alkinyl, may be prepared by the cross-coupling method of Stille (J.K. Stille, Angew. Chem. 1986, *98*, 504-519), Sonogashira (K. Sonogashira et al., Tetrahedron Lett. 1975, 4467-4470), Suzuki (N. Miyaura, A. Suzuki, Chem. Rev. 1995, *95*, 2457-2483) or Heck (R.F. Heck, Org. React. 1982, *27*, 345-390) with optional subsequent hydrogenation. The following reaction scheme illustrates this procedure:



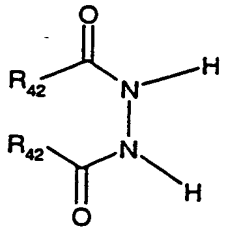
The compounds of formula IV and IVa are either known or may be produced analogously to known methods. Preparation methods for compounds of formula IV are described for example in WO 95/00521. These compounds may be produced e.g. whereby a compound of formula V



(V),

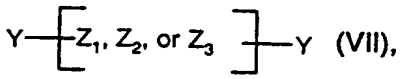
wherein R_{42} signifies hydrogen, C_1-C_4-alkyl, C_1-C_6-alkoxy, C_1-C_6-halogenalkoxy, benzyloxy, preferably hydrogen, methyl, methoxy, ethoxy, trichloroethoxy, *t*-butoxy or benzyloxy and R_4 and R_5 are defined as given in formula I, are heated in an inert solvent in the presence of a base or an acid. Compounds of formula V, wherein R_{42} signifies hydrogen, C_1-C_4-alkyl, C_1-

C_6-alkoxy, C_1-C_6-halogenalkoxy, benzyloxy, preferably hydrogen, methyl, methoxy, ethoxy, trichloroethoxy, *t*-butoxy or benzyloxy and R_4 and R_5 are defined as given in formula I, may be produced for example whereby a compound of formula VI



(VI),

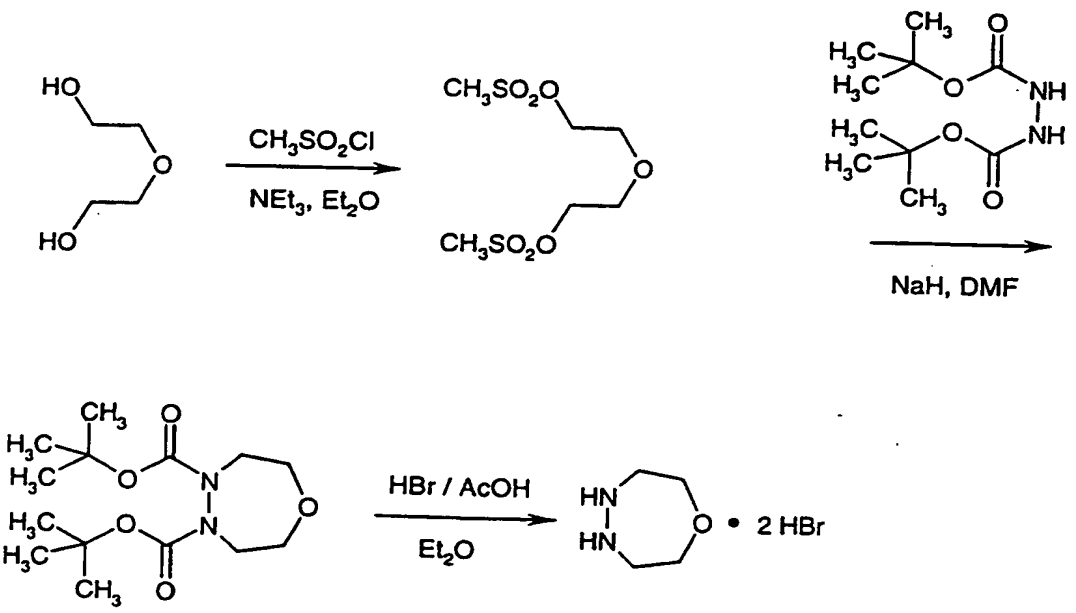
wherein R_{42} signifies hydrogen, C_1-C_4-alkyl, C_1-C_6-alkoxy, C_1-C_6-halogenalkoxy, benzyloxy, preferably hydrogen, methyl, methoxy, ethoxy, trichloroethoxy, *t*-butoxy or benzyloxy, is reacted in the presence of a base and an inert solvent with a compound of formula VII



(VII),

wherein Y signifies halogen, alkyl/aryl sulfonates $-OSO_2R_{43}$, preferably bromine, chlorine, iodine, mesylate ($R_{43} = CH_3$), triflate ($R_{43} = CF_3$) or tosylate (R_{43} = p-tolyl) and Z_1, Z_2 and Z_3 are defined as given in formula I. In formula VII, the free valencies of groups Z_1, Z_2 and Z_3 are each bonded to the group Y. Compounds of formulae VI and VII are known or may be prepared analogously to methods known to those skilled in the art.

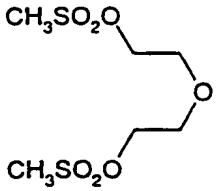
Compounds of formula IV, wherein R_4 and R_5 together are a group Z_2 $-C-R_{14}(R_{15})-C-R_{16}(R_{17})-O-C-R_{18}(R_{19})-C-R_{20}(R_{21})-$ (Z_2), wherein R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21} signify hydrogen, may be produced e.g. in accordance with the following reaction scheme:



The end products of formula I can be isolated in conventional manner by concentrating the reaction mixture and/or removing the solvent by evaporation and by recrystallising or triturating the solid residue in a solvent in which it is not readily soluble, typically an ether, an alkane, an aromatic hydrocarbon or a chlorinated hydrocarbon or by chromatography. Salts of compounds of formula I may be prepared in a known manner. Preparation methods of this kind are described for example in WO 96/21652.

Preparation Examples:

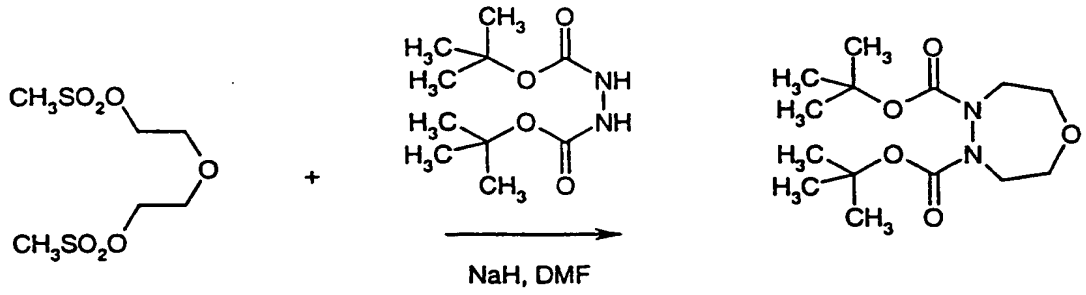
Example P1: Preparation of



(1):

A solution of 177.6 g of methane sulfochloride in 400 ml of diethylether is added dropwise over the course of one hour to a solution, cooled to -10°C, of 80.6 g (0.76 mols) of diethylene glycol and 159.9 g (1.58 mols) of triethylamine in 1500 ml of diethylether, whereby the temperature is maintained at below 5°C. After stirring for 30 minutes at a temperature of 0°C, the cooling means is removed. After 2 hours, 12 ml of triethylamine and 12 ml of methane sulfochloride are added at a temperature of 20°C, and stirring continues for a further 4 hours. The white suspension obtained is subsequently added to a suction filter and the residue washed twice with 300 ml of diethylether. The filtration material is taken up in 2000 ml of ethyl acetate, the suspension stirred for 30 minutes at room temperature and filtration is effected again. The filtrate obtained is concentrated by evaporation and the residue used without further purification for the next reaction. 216.5 g of the desired crude product (1) are obtained in the form of white crystals.

Example P2:

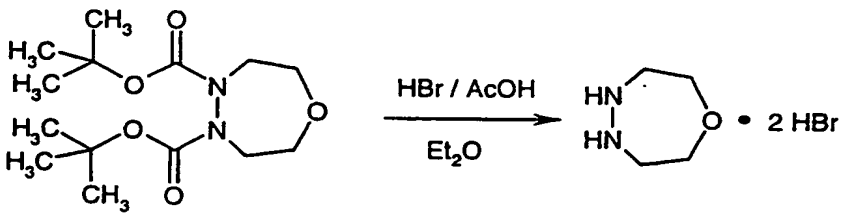


(1) (2) (3)

A solution of 68.78 g (0.30 mols) of (2) in 140 ml of dimethylformamide is added dropwise over the course of 30 minutes to a suspension, cooled to 5°C, of 23.9 g (0.60 mols) of 60% sodium hydride in 500 ml of dimethylformamide. The cooling means is removed and stirring is effected until the reaction mixture has reached a temperature of 20°C. Then, heating is

effected for a short time to a temperature of 30 to 40°C in order to complete the removal of hydrogen. After cooling to a temperature of 0 to 5°C, a solution of 80 g (0.305 mols) of **(1)** in 160 ml of dimethylformamide is added dropwise over the course of 30 minutes, whereby the temperature is maintained at 0 to 5°C. After removing the cooling means and stirring for 3 hours at room temperature, and also for 45 minutes at ca. 40°C, the reaction mixture is added to a mixture of saturated ammonium chloride solution, ice and tert.-butylmethyl ether, the phases are separated and subsequently the organic phase is washed twice with water. After drying the organic phase with sodium sulphate, concentrating by evaporation and further drying at a temperature of 40°C under vacuum, 92.2 g of **(3)** are obtained in the form of a slightly yellow oil. The crude product is used in the next reaction without further purification.

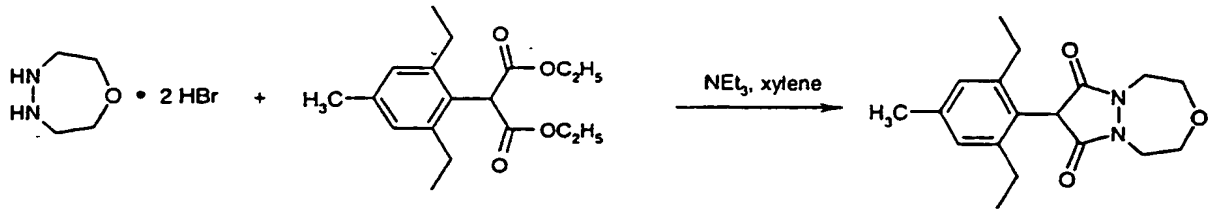
Example P3:



(3) (4)

160.5 ml of a 33% solution of hydrogen bromide in glacial acetic acid is added dropwise over the course of 30 minutes to a solution, cooled to 0°C, of 92.2 g (0.305 mols) of **(3)** in 1200 ml of diethylether. After removing the cooling means and subsequently stirring for 22 hours at 20°C and for 27 hours under reflux, the white suspension obtained is added to a suction filter, washed with diethylether, and then the residue of filtration is dried over P_2O_5 under vacuum at a temperature of 50 to 60°C. The product **(4)** is obtained in a yield of 52.9 g in the form of a white solid.

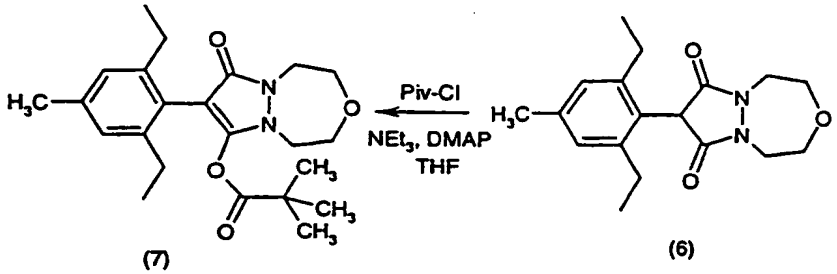
Example P4:



(4) (5) (6)

10.61 ml (76 mmols) of triethylamine are added to a suspension of 4.4 g (16.5 mmols) of **(4)** in 175 ml of xylene, and degassed (4 x vacuum/argon). The yellow suspension is subsequently heated to a temperature of 60°C and stirred for 3 hours. Then, 5.07 g (16.5 mmols) of **(5)** are added and heating effected to a bath temperature of 140°C, in order to continuously distill off the excess triethylamine and the resulting ethanol. After 3 hours, the reaction mixture is cooled to a temperature of 40°C and added to 100 ml of an ice/water mixture. The reaction mixture is rendered alkaline with aqueous 1N sodium hydroxide solution and the aqueous phase (contains the product) is washed twice with ethyl acetate. After twice washing back the organic phase with aqueous 1N sodium hydroxide solution, the aqueous phases are combined, the remaining xylene distilled off and the combined aqueous phases adjusted to pH 2-3 with 4N HCl whilst cooling. The precipitating product is added to a suction filter, the residue of filtration washed with water and briefly with hexane, and then the residue of filtration is dried in a vacuum at a temperature of 60°C over P_2O_5. 4.08 g of **(6)** solid are obtained with a melting point of 189-191°C (decomp.).

Example P5:

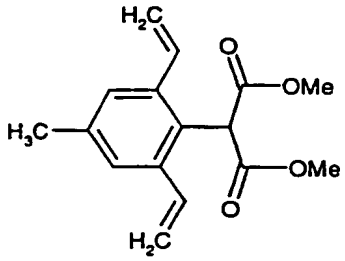


(7) (6)

A catalytic amount of 4-dimethylaminopyridine is added to a solution, cooled to a temperature of 0°C, of 1 g (3.2 mmols) of **(6)** and 0.65 g (6.4 mmols) of triethylamine in

30 ml of tetrahydrofuran. Then, 0.49 g (4.1 mmols) of pivaloyl chloride are added dropwise. After stirring for 30 minutes at a temperature of 0°C, the cooling means is removed and stirring continues for 60 minutes. Subsequently, the reaction mixture is added to saturated aqueous sodium chloride solution and the organic phase is separated. The organic phase is dried over magnesium sulfate, filtered and concentrated by evaporation. After purification by chromatography and recrystallisation from diethylether, 1.07 g of **(7)** are obtained with a melting point of 122 to 123°C.

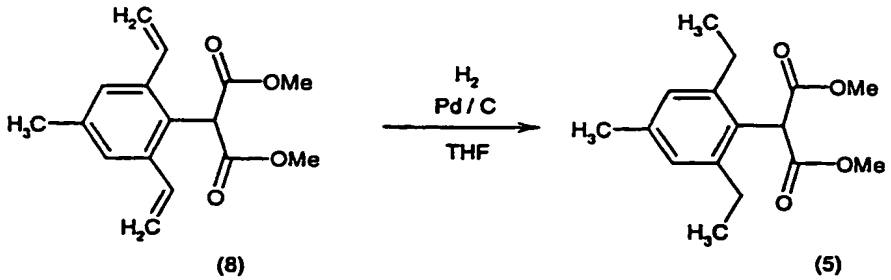
Example P6: Preparation of



(8):

To a solution of 20 g of 2-(2,6-dibromo-4-methylphenyl)-malonic acid dimethylester (known from WO 96/35664) (52.6 mmols) in 400 ml of toluene (3 x degassed, vacuum/argon) are added first of all 36.7 g (0.116 mmols) of tributylvinyl stannane and then 2 g of tetrakis-triphenylphosphine-palladium. The reaction mixture is then stirred for 9 hours at a temperature of 90 to 95°C. After filtration through Hyflo and concentrating on a rotary evaporator, the mixture is purified by chromatography to give 15.3 g of **(8)** in the form of a yellow oil, which is used in the next reaction without further purification.

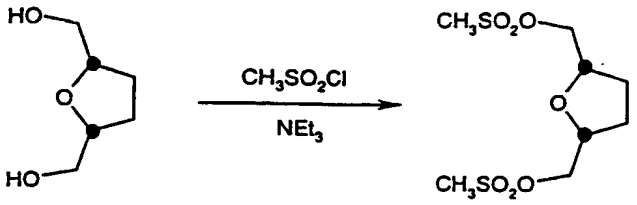
Example P7:



(8) (5)

15.2 g of compound **(8)** obtained in example P6 are hydrogenated at a temperature of 20 to 25°C with hydrogen using a palladium catalyst (carbon as the carrier, 7 g 5% Pd/C) in 160 ml of tetrahydrofuran. When hydrogenation has ended, the product is filtered through Hyflo and the filtrate obtained is concentrated on a rotary evaporator. 13.7 g of **(5)** are obtained in the form of yellow crystals with a melting point of 47 to 49°C.

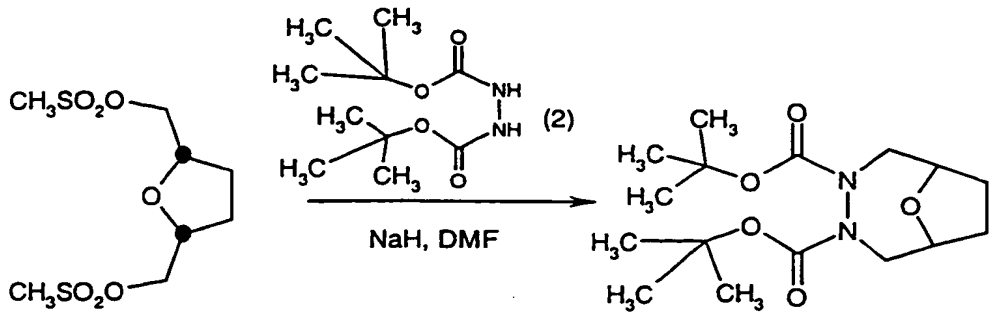
Example P8:



(12) (13)

67.8 g (0.59 mols) of methane sulfochloride are added dropwise to a solution, cooled to 0-3°C, of 37.1 g (0.28 mols) of *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran **(12)** and 65.3 g (0.65 mols) of triethylamine in 400 ml of methylene chloride, whereby the temperature is maintained below 7°C. Stirring is subsequently effected over night at a temperature of 20°C. The white suspension thus obtained is added to a suction filter, the residue washed with methylene chloride and the filtrate concentrated by evaporation. The residue is taken up in ethyl acetate, washed with water (2x) and with saturated aqueous sodium chloride solution (1x), dried (Na_2SO_4) and concentrated. 72.7 g of the dimesylate compound **(13)** are obtained as a crude oil, which is used in the next reaction without further purification.
The educt **(12)** is known in literature: see e.g.K.Naemura et al., Tetrahedron Asymmetry **1993**, *4*, 911-918.

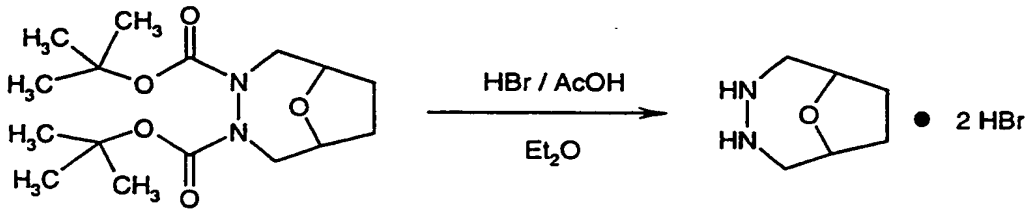
Example P9:



(13) (14)

(14) is obtained as a crude brown oil in analogous manner to example P2, from 21.0 g (0.53 mols) of 60% NaH, 58.4 g (0.25 mols) of **(2)** and 72.5 g (0.25 mols) of dimesylate **(13)** in a total of 840 ml of dimethylformamide. After purification by chromatography, 53.7 g of pure compound **(14)** are obtained as a white solid with a melting point of 81 to 83°C.

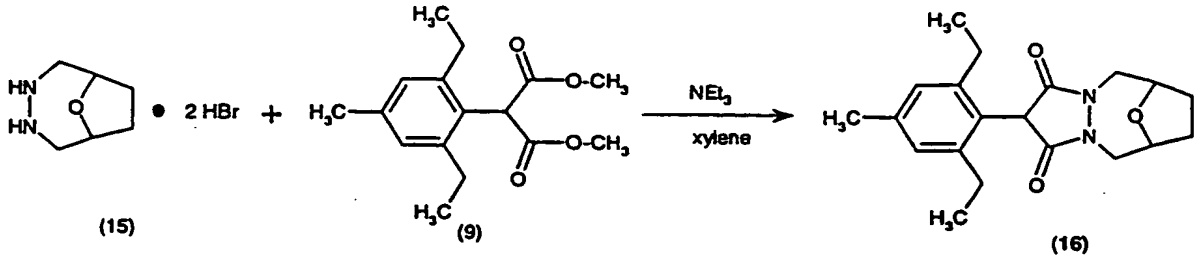
Example P10:



(14) (15)

36.5 g of the bicyclic hydrazine **(15)** are obtained as a solid with a melting point of 262 to 264°C, in analogous manner to example P3, from 53.5 g (0.16 mols) of **(14)** in 800 ml of diethylether and 90 ml of a 33% solution of hydrogen bromide in conc. acetic acid.

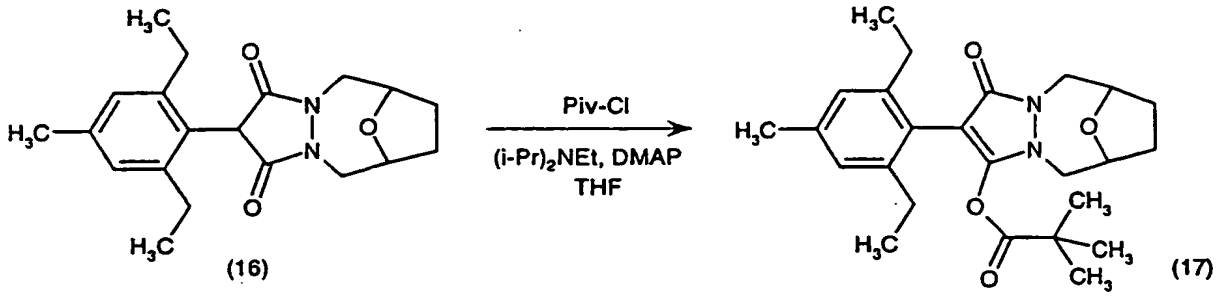
Example P11:



(15) (9) (16)

29.7 g of compound **(16)** are obtained as a solid with a melting point of 287°C, analogously to example P4, from 0.105 mols of the malonate **(9)** and 30.4 g (0.105 mols) of the hydrazine **(15)**.

Example P12:

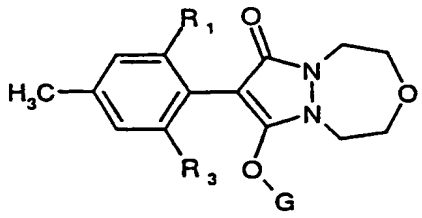


(16) (17)

0.83 g of the pivaloyl ester **(17)** are obtained as a solid with a melting point of 141-143°C, analogously to example P9, from 1.1 g (3.2 mmols) of **(16)**.

If a formula is illustrated for the substituent G, then the left side of this formula is the connection point to the oxygen atom of the heterocycle. The remaining terminal valencies represent methyl groups.

Table 1: Compounds of formula Ie:

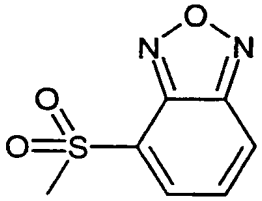
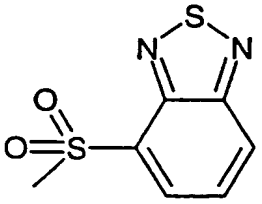
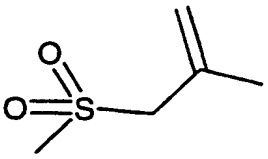


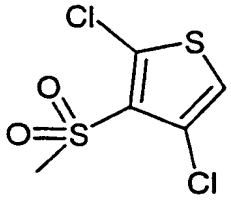
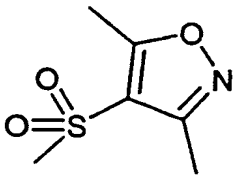
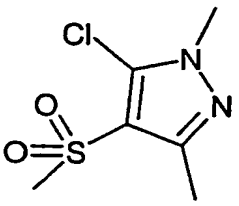
(Ie)

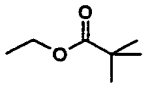
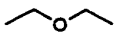
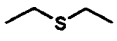
Comp. No.	R_1	R_3	G	phys. data
1.001	CH_3	OCH_3	H	
1.002	CH_3	OCH_3	$C(O)C(CH_3)_3$	
1.003	CH_3	OCH_3	$C(O)OCH_2CH_3$	
1.004	CH_2CH_3	CH_3	H	m.p. 182-

Comp. No.	R_1	R_3	G	phys. data
				185°C
1.005	CH_2CH_3	CH_3	$C(O)C(CH_3)_3$	m.p. 110-113°C
1.006	CH_2CH_3	CH_3	$C(O)OCH_2CH_3$	
1.007	CH_2CH_3	CH_2CH_3	H	m.p. 189-191°C
1.008	CH_2CH_3	CH_2CH_3	$C(O)C(CH_3)_3$	m.p. 122-124°C
1.009	CH_2CH_3	CH_2CH_3	$C(O)OCH_2CH_3$	m.p. 114-116°C
1.010	$CH=CH_2$	CH_3	H	m.p. 165-170°C
1.011	$CH=CH_2$	CH_3	$C(O)C(CH_3)_3$	m.p. 111-113°C
1.012	$CH=CH_2$	CH_2CH_3	H	
1.013	$CH=CH_2$	$CH=CH_2$	H	
1.014	$CH=CH_2$	$CH=CH_2$	$C(O)C(CH_3)_3$	
1.015	$C\equiv CH$	CH_3	H	m.p. 179-184°C
1.016	$C\equiv CH$	CH_3	$C(O)C(CH_3)_3$	m.p. 109-111°C
1.017	$C\equiv CH$	CH_3	$C(O)OCH_2CH_3$	
1.018	$C\equiv CH$	CH_2CH_3	H	m.p. 189-193°C
1.019	$C\equiv CH$	CH_2CH_3	$C(O)C(CH_3)_3$	
1.020	$C\equiv CH$	CH_2CH_3	$C(O)OCH_2CH_3$	
1.021	$C\equiv CH$	$C\equiv CH$	H	m.p. 300°C
1.022	$C\equiv CH$	$C\equiv CH$	$C(O)C(CH_3)_3$	m.p. 183-185°C
1.023	$C\equiv CH$	$C\equiv CH$	$C(O)OCH_2CH_3$	
1.024	$C\equiv CH$	$CH=CH_2$	H	

Comp. No.	R_1	R_3	G	phys. data
1.025	$C\equiv CCH_3$	CH_3	H	m.p. 179-181°C
1.026	$C\equiv CCH_3$	CH_3	$C(O)C(CH_3)_3$	m.p. 128-129°C
1.027	$C\equiv CCH_3$	CH_3	$C(O)OCH_2CH_3$	
1.028	$C\equiv CCH_3$	CH_2CH_3	H	
1.029	$C\equiv CCH_3$	CH_2CH_3	$C(O)C(CH_3)_3$	
1.030	$C\equiv CCH_3$	$C\equiv CCH_3$	H	
1.031	$C\equiv CCH_3$	$C\equiv CCH_3$	$C(O)C(CH_3)_3$	
1.032	$CH_2CH_2CH_3$	CH_3	H	m.p. 136-138°C
1.033	$CH_2CH_2CH_3$	CH_3	$C(O)C(CH_3)_3$	m.p. 65-67°C
1.034	$CH_2CH_2CH_3$	CH_3	$C(O)OCH_2CH_3$	
1.035	$CH_2CH_2CH_3$	CH_2CH_3	H	
1.036	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$	H	
1.037	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$	$C(O)C(CH_3)_3$	
1.038	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$	$C(O)OCH_2CH_3$	
1.039	$CH_2CH_2CH_3$	$C\equiv CH$	H	
1.040	$CH(CH_3)_2$	CH_3	H	m.p. 214-216°C
1.041	$CH(CH_3)_2$	CH_3	$C(O)C(CH_3)_3$	m.p. 148-151°C
1.042	$CH(CH_3)_2$	CH_2CH_3	H	
1.043	$CH(CH_3)_2$	$C\equiv CH$	H	
1.044		CH_3	H	
1.045		CH_2CH_3	H	
1.046		$C\equiv CH$	H	
1.047	$CH_2CH=CH_2$	CH_3	H	

Comp. No.	R_1	R_3	G	phys. data
1.048	$CH_2CH=CH_2$	CH_2CH_3	H	
1.049	$CH_2CH=CH_2$	C≡CH	H	
1.050	$CH_2CH_2CH_2CH_3$	CH_3	H	
1.051	CH_3O-	CH_2CH_3	H	
1.052	CH_3O-	CH_2CH_3	$C(O)C(CH_3)_3$	
1.053	CH_2CH_3	CH_2CH_3	$SO_2CH(CH_3)_2$	
1.054	CH_2CH_3	CH_2CH_3	SO_2CH_3	crystalline
1.055	CH_2CH_3	CH_2CH_3	$SO_2CH(CH_3)_2$	
1.056	CH_2CH_3	CH_2CH_3	SO_2CF_3	
1.057	CH_2CH_3	CH_2CH_3	$SO_2CH_2CH_3$	
1.058	CH_2CH_3	CH_2CH_3	$SO_2CH_2\ CH(CH_3)_2$	wax
1.059	CH_2CH_3	CH_2CH_3	$SO_2CH_2CH_2Cl$	
1.060	CH_2CH_3	CH_2CH_3	$SO_2CH=CH_2$	wax
1.061	CH_2CH_3	CH_2CH_3	$SO_2CH_2CH_2Br$	
1.062	CH_2CH_3	CH_2CH_3		F.:204-205
1.063	CH_2CH_3	CH_2CH_3		F.:203-204
1.064	CH_2CH_3	CH_2CH_3	SO_2-benzyl	F.:157-158
1.065	CH_2CH_3	CH_2CH_3		wax

Comp. No.	R_1	R_3	G	phys. data
1.066	CH_2CH_3	CH_2CH_3	$SO_2CH_2CH_2$ CH_2Cl	wax
1.067	CH_2CH_3	CH_2CH_3		F.: 126
1.068	CH_2CH_3	CH_2CH_3		F.: 146
1.069	CH_2CH_3	CH_2CH_3		F.: 82-85
1.070	CH_2CH_3	CH_2CH_3	$SO_2CH_2CH=CH_2$	
1.071	C≡CH	CH_2CH_3	SO_2CH_3	
1.072	C≡CH	CH_2CH_3	$SO_2CH(CH_3)_2$	
1.073	C≡CH	CH_2CH_3	$SO_2CH_2CH_2Cl$	
1.074	C≡CH	CH_2CH_3	SO_2CF_3	
1.075	C≡CH	CH_2CH_3	$SO_2CH=CH_2$	
1.076	C≡CH	OCH_3	-H	m.p. 202-204
1.077	C≡CH	OCH_3	$C(O)C(CH_3)_3$	m.p. 204-206
1.078	$C≡CSi(CH_3)_3$	OCH_3	$C(O)C(CH_3)_3$	m.p. 169-171
1.079	$C≡CSi(CH_3)_3$	OCH_3	-H	m.p. 173-174
1.080	Br	OCH_3	-H	m.p. 217-219

Comp. No.	R_1	R_3	G	phys. data
1.081	Br	OCH_3	$C(O)C(CH_3)_3$	m.p. 173-175
1.082	CH_2CH_3	CH_2CH_3	$C(O)C(CH_3)_2CH_2CH_3$	m.p. 122-124°C
1.083	CH_2CH_3	CH_2CH_3	$CON(CH_2CH_3)_2$	m.p. 82-84
1.084	CH_2CH_3	$C(O)CH_3$	$C(O)C(CH_3)_2CH_2CH_3$	m.p. 138-139°C
1.085	CH_2CH_3	$C(O)CH_3$		
1.086	CH_2CH_3	$C(O)CH_3$		
1.087	CH_2CH_3	$C(O)CH_3$		
1.088	CH_2CH_3	$C(O)CH_3$		

The invention also relates to a method for the selective control of weeds in crops of cultivated plants, which comprises treating the cultivated plants, the seeds or seedlings or the crop area thereof, with a) a herbicidally effective amount of a herbicide of formula I, b) a herbicidally synergistic amount of at least one herbicide selected from the classes of phenoxy-phenoxypropionic acids, hydroxylamines, sulfonylureas, imidazolinones, pyrimidines, triazines, ureas, PPO, chloroacetanilides, phenoxyacetic acids, triazinones, dinitroanilines, azinones, carbamates, oxyacetamides, thiolcarbamates, azole-ureas, benzoic acids, anilides, nitriles, triones and sulfonamides, as well as the herbicides amitrol, benfuresate, bentazone, cinmethylin, clomazone, chlopyralid, difenzoquat, dithiopyr, ethofumesate, flurochloridone, indanofane, isoxaben, oxaziclomefone, pyridate, pyridafol, quinchlorac, quinmerac, tridiphane, flamprop and glufosinate; and optionally
c) to antagonise the herbicide, an antidotally effective amount of a safener selected from cloquintocet, an alkali, alkaline earth, sulfonium or ammonium cation of cloquintocet, cloquintocet-mexyl, mefenpyr, an alkali, alkaline earth, sulfonium or ammonium cation of mefenpyr and mefenpyr-diethyl; and/or
d) an additive comprising an oil of vegetable or animal origin, a mineral oil, the alkylesters thereof or mixtures of these oils and oil derivatives.

The cultivated plants which may be protected against the harmful action of the above-mentioned herbicides by the safeners cloquintocet, an alkali, alkaline earth, sulfonium or ammonium cation of cloquintocet, or cloquintocet-mexyl, mefenpyr, an alkali, alkaline earth, sulfonium or ammonium cation of mefenpyr, or mefenpyr-diethyl, are in particular cereals, cotton, soya, sugar beet, sugar cane, plantations, rape, maize and rice, especially maize and cereals. Crops will also be understood to mean those crops that have been made tolerant to herbicides or classes of herbicides by conventional breeding or genetic engineering methods. These are e.g. IMI Maize, Poast Protected Maize (sethoxydim tolerance), Liberty Link Maize, B.t./Liberty Link Maize, IMI/Liberty Link Maize, IMI/Liberty Link /B.t. Maize, Roundup Ready Maize and Roundup Ready/B.t. Maize.

The weeds to be controlled may be both dicot weeds, and preferably monocot weeds, for example the monocot weeds *Avena, Agrostis, Phalaris, Lolium, Bromus, Alopecurus, Setaria, Digitaria Brachiaria, Echinochloa, Panicum, Sorghum hal./bic., Rottboellia, Cyperus, Brachiaria, Echinochloa, Scirpus, Monochoria,* and *Sagittaria* and the dicot weeds *Sinapis, Chenopodium, Stellaria, Galium, Viola, Veronica, Matricaria, Papaver, Solanum Abutilon, Sida, Xanthium, Amaranthus, Ipomoea* and *Chrysanthemum.*

Crop areas will be understood as meaning the areas already under cultivation with the cultivated plants or seeds thereof, as well as the areas intended for cropping with said cultivated plants.

Depending on the end use, a safener according to the invention can be used for pretreating seeds of the crop plants (dressing of seeds or seedlings) or it can be incorporated in the soil before or after sowing. It can, however, also be applied by itself alone or together with the herbicide and the oil additive postemergence. Treatment of the plant or the seeds with the safener can therefore in principle be carried out irrespective of the time of application of the herbicide. Treatment of the plant can, however, also be carried out by simultaneous application of the herbicide, oil additive and safener (e.g. as tank mixture). The concentration of safener with respect to the herbicide will depend substantially on the mode of application. Where a field treatment is carried out either by using a tank mixture with a combination of safener and herbicide or by separate application of safener and herbicide, the ratio of herbicide to safener will usually be from 100:1 to 1:10, preferably 20:1 to 1:1. In

field treatment it is usual to apply 0.001 to 1.0 kg/ha, preferably 0.001 to 0.25 kg/ha, of safener.

The concentration of herbicide is usually in the range from 0.001 to 2 kg/ha, but will preferably be from 0.005 to 1 kg/ha.

In the composition of the invention, the compound of formula I is present in relation to the second herbicide in a weight ratio of 1 : 100 to 1000 : 1.

In the composition according to the invention, the application rates of oil additive are as a rule between 0.01 and 2% based on the spray mixture. For example, the oil additive can be added to the spray tank in the desired concentration after preparation of the spray mixture.

Preferred oil additives contain mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow.

Particularly preferred oil additives contain alkylesters of higher fatty acids (C_8-C_{22}), especially the methyl derivatives of C_{12}-C_{18} fatty acids, for example the methylesters of lauric acid, palmitic acid and oleic acid. These esters are known as methyl laurate (CAS-111-82-0), methyl palmitate (CAS-112-39-0) and methyl oleate (CAS-112-62-9).

The application and efficacy of the oil additives can be improved by combining them with surface-active substances, such as non-ionic, anionic or cationic surfactants. Examples of suitable anionic, non-ionic, and cationic surfactants are listed in WO 97/34485 on pages 7 and 8.

Preferred surface-active substances are anionic surfactants of the dodecylbenzene sulfonate type , especially the calcium salts thereof, as well as non-ionic surfactants of the fatty alcohol ethoxylate type. Especially preferred are ethoxylated C_{12}-C_{22}-fatty alcohols with a degree of ethoxylation of between 5 and 40. Examples of commercially available, preferred surfactants are the Genapol types (Clariant AG, Muttenz, Switzerland).
The concentration of surface-active substances in relation to the total additive is in general between 1 and 30% by weight.

Examples of oil additives, which comprise mixtures of oils or mineral oils, or the derivatives thereof, with surfactants, are Edenor ME SU®, Emery 2231® (Henkel Tochtergesellschaft Cognis GMBH, DE), Turbocharge® (Zeneca Agro, Stoney Creek, Ontario , CA) or, most preferably, Actipron® (BP Oil UK Limited, GB).

Furthermore, the addition of an organic solvent to the oil additive/surfactant mixture can effect a further increase in efficacy. Suitable solvents are for example the Solvesso® (ESSO) or Aromatic Solvent® (Exxon Corporation) types.
The concentration of such solvents may be from 10 to 80% by weight of the total weight.

Oil additives of this kind, which are also described for example in US-A-4.834.908, are particularly preferred for the composition according to the invention. A most particularly preferred oil additive is known under the name MERGE® which can be obtained from the BASF Corporation and is basically described for example in US-A-4.834.908 in column 5, as example COC-1. A further preferred oil additive according to the invention is SCORE® (Novartis Crop Protection Canada).

The compositions of this invention are suitable for all methods of application commonly used in agriculture, including preemergence application, postemergence application and seed dressing.

For seed dressing, 0.001 to 10 g of safener/kg of seeds, preferably 0.05 to 6 g of safener/kg of seeds, is usually applied. If the safener is used in liquid form shortly before sowing to effect soaking, then it is preferred to use safener solutions that contain the active ingredient in a concentration of 1 to 10000 ppm, preferably of 10 to 1000 ppm.

For application, it is preferred to process the safeners according to the invention, or mixtures of the safeners and the herbicides and the oil additives, conveniently together with the customary assistants of formulation technology to formulations, typically to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates or microcapsules.

Such formulations are described, for example, in WO 97/34485 on pages 9 to 13. The formulations are prepared in known manner, conveniently by homogeneously mixing and/or grinding the active ingredients with liquid or solid formulation assistants, typically solvents or solid carriers. Surface-active compounds (surfactants) may additionally be used for preparing the formulations. Solvents and solid carriers that are suitable for this purpose are described in WO 97/34485 on page 6.

Depending on the herbicide of formula I to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties. Examples of suitable anionic, non-ionic, and cationic surfactants are listed in WO 97/34485 on pages 7 and 8. Also the surfactants customarily for the art of formulation and described, *inter alia*, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch" (Handbook of Surfactants), Carl Hanser Verlag, Munich/Vienna, 1981, and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81 are suitable for manufacture of the herbicides according to the invention.

The herbicidal compositions will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of compound mixture of the compound of formula I, the second synergistically active herbicide and optionally the safeners according to the invention, 0 to 2% by weight of the oil additive according to the invention, from 1 to 99.9% by weight of a solid or liquid formulation assistant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant. Whereas it is customarily preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The compositions may also contain further ingredients, such as: stabilisers, e.g. where appropriate epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil, or soybean oil); antifoams, typically silicone oil; preservatives; viscosity regulators; binders; tackifiers; as well as fertilisers or other chemical agents. Different methods and techniques may suitably be used for applying the safeners according to the invention or compositions containing them for protecting cultivated plants from the harmful effects of herbicides of formula I, conveniently the following:

i) Seed dressing

a) Dressing the seeds with a wettable powder formulation of the active ingredient of the safeners according to the invention by shaking in a vessel until uniformly distributed on the surface of the seeds (dry treatment), In this instance, approximately 1 to 500 g of active ingredient of the safeners according to the invention (4 g to 2 kg of wettable powder) is used per 100 kg of seeds.

b) Dressing seeds with an emulsifiable concentrate of the safeners according to the invention by method a) (wet treatment).

c) Dressing by immersing the seeds in a mixture containing 100–1000 ppm of safeners according to the invention for 1 to 72 hours and where appropriate subsequently drying them (seed soaking).

In keeping with the natural environment, the preferred method of application is either seed dressing or treatment of the germinated seedlings, because the safener treatment is fully concentrated on the target crop. Usually 1 to 1000 g, preferably 5 to 250 g, of safener is used per 100 kg of seeds. However, depending on the method employed, which also permits the use of other chemical agents or micronutrients, the concentrations may deviate above or below the indicated limit values (repeat dressing).

ii) Application as a tank mixture

A liquid formulation of a mixture of safener and herbicide (reciprocal ratio from 20:1 to 1:100) is used, the concentration of herbicide being from 0.005 to 5.0 kg/ha. The oil additive may be added to the tank mixture in an amount of preferably 0.01 to 2% by weight. This tank mixture is applied before or after sowing.

iii) Application in the furrow

The safener formulated as emulsifiable concentrate, wettable powder or granulate is applied to the open furrow in which the seeds have been sown. After covering the furrow, the herbicide is applied pre-emergence in conventional manner, optionally in combination with the oil additive.

iv) Controlled release of compound

A solution of the safener is applied to a mineral granular carrier or to a polymerised granulate (urea/formaldehyde) and then dried. A coating can then be applied (coated granules) that allows the active ingredient to be released at a controlled rate over a specific period of time.

Particularly preferred formulations are made up as follows:
% = percent by weight; compound mixture means the mixture of compound of formula I with the synergistically active second herbicide and optionally with the safeners according to the invention and/or the oil additives)

Emulsifiable concentrates:

Compound mixture:	1 to 90 %, preferably 5 to 20 %
surfactant:	1 to 30 %, preferably 10 to 20 %
liquid carrier:	5 to 94 %, preferably 70 to 85 %

Dusts:

Compound mixture:	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

Compound mixture:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surfactant:	1 to 40 %, preferably 2 to 30 %

Wettable powders:

Compound mixture:	0.5 to 90 %, preferably 1 to 80 %
surfactant:	0.5 to 20 %, preferably 1 to 15 %
solid carrier:	5 to 95 %, preferably 15 to 90 %

Granulates:

Compound mixture:	0.1 to 30 %, preferably 0.1 to 15 %
solid carrier:	99.5 to 70 %, preferably 97 to 85 %

The invention is illustrated by the following non-limitative Examples.

Formulation examples for mixtures of herbicides and, where appropriate, safeners and oil additive (% = p rcent by weight)

F1. Emulsifiable concentrates	a)	b)	c)	d)

compound mixture	5 %	10 %	25 %	50 %
calcium dodecylbenzene sulphonate	6 %	8 %	6 %	8 %
polyethoxylated castor oil (36 mol EO)	4 %	-	4 %	4 %
octylphenol polyglycol ether (7-8 mol EO)	-	4 %	-	2 %
cyclohexanone	-	-	10 %	20 %
aromatic hydrocarbon mixture C_9-C_{12}	85 %	78 %	55 %	16 %

Emulsions of any desired concentration can be prepared by diluting such concentrates with water.

F2. Solutions	a)	b)	c)	d)
compound mixture	5 %	10 %	50 %	90 %
1-methoxy-3-(3-methoxy-propoxy)-propane	-	20 %	20 %	-
polyethylene glycol (MW 400)	20 %	10 %	-	-
N-Methyl-2-pyrrolidone	-	-	30 %	10 %
aromatic hydrocarbon mixture C_9-C_{12}	75 %	60 %	-	-

The solutions are suitable for use in the form of microdrops.

F3. Wettable powders	a)	b)	c)	d)
compound mixture	5 %	25 %	50 %	80 %
sodium ligninsulphonate	4 %	-	3 %	-
sodium lauryl sulphate	2 %	3 %	-	4 %
sodium diisobutylnaphthalene sulfonate	-	6 %	5 %	6 %
octylphenol polyglycol ether (7-8 mol EO)	-	1 %	2 %	-
highly dispersed silicic acid	1 %	3 %	5 %	10 %
kaolin	88 %	62 %	35 %	-

The compound is throughly mixed with the adjuvants and this mixture is ground in a suitable mill to give wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granulates	a)	b)	c)
compound mixture	0.1 %	5 %	15 %

highly dispersed silicic acid	0.9 %	2 %	2 %
Inorganic carrier	99.0 %	93 %	83 %
(Æ 0.1–1 mm)			
such as $CaCO_3$ or SiO_2			

The compound mixture is dissolved in methylene chloride, the solution is sprayed on to the carrier, and the solvent is removed under vacuum.

F5. Coated granulates	a)	b)	c)
compound mixture	0.1 %	5 %	15 %
polyethylene glycol (MW 200)	1.0 %	2 %	3 %
highly dispersed silicic acid	0.9 %	1 %	2 %
inorganic carrier	98.0 %	92 %	80 %
(Æ 0.1–1 mm)			
such as $CaCO_3$ or SiO_2			

The finely ground active substance is uniformly applied in a mixer to the carrier moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

F6. Extruder granulates	a)	b)	c)	d)
compound mixture	0.1 %	3 %	5 %	15 %
sodium ligninsulphonate	1.5 %	2 %	3 %	4 %
carboxymethylcellulose	1.4 %	2 %	2 %	2 %
kaolin	97.0 %	93 %	90 %	79 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. This mixture is extruded and then dried in a stream of air.

F7. Dusts	a)	b)	c)
compound mixture	0.1 %	1 %	5 %
talc	39.9 %	49 %	35 %
kaolin	60.0 %	50 %	60 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding on a suitable mill.

F8. Suspension concentrates	a)	b)	c)	d)
compound mixture	3 %	10 %	25 %	50 %
ethylene glycol	5 %	5 %	5 %	5 %
nonylphenol polyglycol ether	-	1 %	2 %	-
(15 mol EO)				
sodium ligninsulphonate	3 %	3 %	4 %	5 %

carboxymethylcellulose	1 %	1 %	1 %	1 %
37% aqueous formaldehyde solution	0.2 %	0.2 %	0.2 %	0.2 %
silicone oil emulsion	0.8 %	0.8 %	0.8 %	0.8 %
water	87 %	79 %	62 %	38 %

The finely ground active substance is intimately mixed with the adjuvants. In this way, a suspension concentrate is obtained from which suspensions of any desired concentration can be prepared by dilution with water.

It is often expedient to formulate herbicides (optionally in combination with the oil additive) and the safeners separately and not to combine them until shortly before application in the applicator in the desired mixing ratio in the form of a "tank mix" in water. The herbicides and the safener may also be formulated individually and combined shortly before application in the applicator in the desired mixing ratio in the form of a "tank mix" in water, and then to add the oil additive.

The selective herbicidal action of the compositions according to the invention is depicted in the following examples.

Biological Examples

Example B1: Postemergence test:

The test plants are raised in pots under greenhouse conditions until reaching a post-application stage. Standard soil is used as the growing medium. In a post-emergence stage, the herbicides are applied to the test plants both on their own and in a mixture with safeners and/or oil additives, or are applied to crop plants raised from seed previously dressed with safeners. They are applied as an emulsion [prepared from an emulsion concentrate (example F1, c)] of the test substances. The rates of application depend on the optimum dosages determined under field or greenhouse conditions. Evaluation of the tests is made after 2 to 4 weeks (% action = completely dead; 0% action = no phytotoxic action). The oil additive used is ACTIPRON® in a concentration of 0.5% by weight of the spray liquor.

Table B1: Postemergence herbicidal action on *Alopecurus*

Compound mixture	concentration in g/ha	phytotoxic action on *Alopecurus* in %
Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	40 + 10	40
comp. no. 1.007 + Cloquintocet-mexyl + ACTIPRON®	15 + 3.75	0
comp. no. 1.007 + Cloquintocet-mexyl + ACTIPRON®	30 + 7.5	0
comp. no. 1.007 + Cloquintocet-mexyl + ACTIPRON®	45 + 11.25	0
comp. no. 1.007 + Cloquintocet-mexyl + ACTIPRON®	60 + 15	0
comp. no. 1.007 + Cloquintocet-mexyl + ACTIPRON®	125 + 31.25	40
comp. no. 1.007 + Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	15 + 15 +3.75	92
comp. no. 1.007 + Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	15 + 20 + 5	96
comp. no. 1.007 + Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	30 + 15 + 7.5	94
comp. no. 1.007 +	30 + 20 + 7.5	96

Compound mixture	concentration in g/ha	phytotoxic action on *Alopecurus* in %
Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®		
comp. no. 1.007 + Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	45 + 15 + 11.25	92
comp. no. 1.007 + Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	45 + 20 + 11,25	96
comp. no. 1.007 + Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	60 + 15 + 15	98
comp. no. 1.007 + Clodinafop-propargyl + Cloquintocet-mexyl + ACTIPRON®	60 + 20 + 15	99

The tests show that the herbicide component Clodinafop-propargyl in combination with the safener Cloquintocet-mexyl and the oil additive ACTIPRON® achieve herbicidal action of only 40% on *Alopecurus* with a total application rate of herbicide/safener of 40 g/ha. The compound of formula I (no. 1.007) in combination with the safener Cloquintocet-mexyl and the oil additive ACTIPRON® achieve no herbicidal action at all on *Alopecurus* at 4 tested application rates, and only 40% with the highest application rate (125 + 31.25 g/ha). Surprisingly, the combination according to the invention of the herbicide of formula I (no. 1.007) with Clodinafop-propargyl, the safener Cloquintocet-mexyl and the oil additive ACTIPRON® is, however, in a position to almost totally eradicate *Alopecurus* at all the tested application rates (92 to 99% action).

A similar effect is observed if the oil additive MERGE® is used instead of ACTIPRON®.

Example B2: Postemergence test:

The test plants are raised in pots under greenhouse conditions until reaching a post-application stage. Standard soil is used as the growing medium. In a postemergence stage, the herbicides are applied to the test plants both on their own and in a mixture with safeners and/or oil additives, or are applied to crop plants raised from seed previously dressed with safeners. They are applied as an emulsion [prepared from an emulsion concentrate (example F1, c)] of the test substance. The rates of application depend on the optimum dosages determined under field or greenhouse conditions. Evaluation of the tests is made after 2 to 4 weeks (% action = completely dead; 0% action = no phytotoxic action). The oil additive used is MERGE® in a concentration of 0.7% by weight of the spray liquor.

Table B2.1: postemergence herbicidal action on weeds in wheat crops, co-herbicide: Triasulfuron:

Compound mixture concentration in g/ha	wheat	Agrostis	Avena	Lolium	Setaria
comp. 1.008 (30 g/ha) + Cloquintocet-mexyl (8 g/ha) + Triasulfuron (7 g/ha)	0	80	40	80	50
comp. 1.008 (30 g/ha) + Cloquintocet-mexyl (8 g/ha) + MERGE + Triasulfuron (7 g/ha)	0	90	100	100	90

Table B2.2: postemergence herbicidal action on weeds in wheat crops, co-herbicide: Fenoxaprop-ethyl:

Compound mixture concentration in g/ha	wheat	Agrostis	Avena	Lolium	Setaria
comp. 1.008 (125 g/ha) + Cloquintocet-mexyl (30 g/ha) +Fenoxaprop-ethyl (1.2 g/ha)	0	100	100	98	98
comp. 1.008 (125 g/ha) +Cloquintocet-mexyl (30 g/ha) + MERGE + Fenoxaprop-ethyl (1.2 g/ha)	0	100	100	100	100

Table B2.3: postemergence herbicidal action on weeds in wheat crops, co-herbicide: Tralkoxydim:

Compound mixture concentration in g/ha	wheat	Agrostis	Avena	Lolium	Setaria
comp. 1.008 (30 g/ha) + Cloquintocet-mexyl (8 g/ha) + Tralkoxydim (250 g/ha)	0	98	100	90	80
comp. 1.008 (30 g/ha) + Cloquintocet-mexyl (8 g/ha) + MERGE + Tralkoxydim (250 g/ha)	0	100	100	100	98

Table B2.4: postemergence herbicidal action on weeds in wheat crops, co-herbicide: Tralkoxydim:

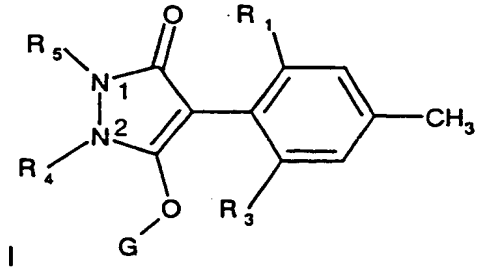
Compound mixture concentration in g/ha	wheat	Agrostis	Avena	Lolium	Setaria
comp. 1.008 (30 g/ha) + Cloquintocet-mexyl (8 g/ha) + Tralkoxydim (125 g/ha)	0	95	95	80	80
comp. 1.008 (30 g/ha + Cloquintocet-mexyl (8 g/ha) + MERGE + Tralkoxydim (125 g/ha)	0	98	98	100	98

From Tables B2.1 to B 2.4, it can be deduced that the addition of the oil additive MERGE® to a mixture of 2 herbicides and one safener leads to a surprising increase in herbicidal action on the weeds without harming the crops.

What is claimed is:

1. A selective herbicidal composition comprising, in addition to customary inert formulation assistants, as the active ingredient a mixture of

a) a herbicidally effective amount of a compound of formula I



(I)

wherein

R_1 and R_3 independently of one another are halogen, nitro, cyano, C_1-C_4-alkyl, C_2-C_4-alkenyl, C_2-C_4-alkinyl, C_1-C_4-halogenalkyl, C_2-C_6-halogenalkenyl, C_3-C_6-cycloalkyl, halogen-substituted C_3-C_6-cycloalkyl, C_2-C_6-alkoxyalkyl, C_2-C_6-alkylthioalkyl, hydroxy, mercapto, C_1-C_6-alkoxy, C_3-C_6-alkenyloxy, C_3-C_6-alkinyloxy, carbonyl, carboxyl, C_1-C_4-alkylcarbonyl, C_1-C_4-hydroxyalkyl, C_1-C_4-alkoxycarbonyl, C_1-C_4-alkylthio, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, amino, C_1-C_4-alkylamino or di-(C_1-C_4-alkyl)-amino;

R_4 and R_5 together signify a group

$-C-R_6(R_7)-O-C-R_8(R_9)-C-R_{10}(R_{11})-C-R_{12}(R_{13})-$ (Z_1),

$-C-R_{14}(R_{15})-C-R_{16}(R_{17})-O-C-R_{18}(R_{19})-C-R_{20}(R_{21})-$ (Z_2), or

$-C-R_{22}(R_{23})-C-R_{24}(R_{25})-C-R_{26}(R_{27})-O-C-R_{28}(R_{29})-$; ($Z_3$) ;

wherein R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, R_{26}, R_{27}, R_{28}, and R_{29} independently of one another are hydrogen, halogen, C_1-C_4-alkyl or C_1-C_4-halogenalkyl, whereby an alkylene ring, which together with the carbon atoms of groups Z_1, Z_2 or Z_3 contains 2 to 6 carbon atoms and may be interrupted by oxygen, may be either anellated or spiro-linked to the carbon atoms of groups Z_1, Z_2 or Z_3, or this alkylene ring overbridges at least one ring atom of groups Gruppen Z_1, Z_2 or Z_3 ;

G is hydrogen, $-C(X_1)-R_{30}$, $-C(X_2)-X_3-R_{31}$, $-C(X_4)-N(R_{32})-R_{33}$, $-SO_2-R_{34}$, an alkaline, alkaline earth, sulfonium or ammonium cation or $-P(X_5)(R_{35})-R_{36}$ or $-CH_2-X_6-R_{37}$;

X_1, X_2, X_3, X_4, X_5 and X_5 independently of one another, are oxygen or sulfur;

R_{30}, R_{31}, R_{32} und R_{33} independently of one another, are hydrogen,

C_1-C_{10}-alkyl, C_1-C_{10}-halogenalkyl, C_1- C_{10}-cyanoalkyl, C_1- C_{10}-nitroalkyl, C_1- C_{10}-aminoalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7-cycloalkyl-C_1-C_5-alkyl, C_2-C_{10}-alkoxy-alkyl, C_4- C_{10}-alkenyloxy-alkyl, C_4- C_{10}-alkinyloxy-alkyl, C_2- C_{10}-alkylthio-alkyl, C_1-C_5-alkysulfoxyl- C_1-C_5-alkyl, C_1-C_5-alkylsulfonyl-C_1-C_5-alkyl, C_2-C_8-alkylideneamino-oxy-C_1-C_5-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_5-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_5-alkyl, C_1-C_5-amino-carbonyl-C_1-C_5-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_5-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_5-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_5-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl-C_1-C_5-alkyl, heteroaryl- C_1-C_5-alkyl, phenoxy- C_1-C_5-alkyl, heteroaryloxy- C_1-C_5-alkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, phenyl; or phenyl substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or heteroaryl or heteroarylamino; heteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diheteroarylamino, diheteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; phenylamino, phenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diphenylamino, diphenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkylamino, C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; di-C_3-C_7-cycloalkylamino, di-C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkoxy or C_3-C_7-cycloalkoxy substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro;

R_{34}, R_{35} and R_{36} independently of one another, are hydrogen, C_1-C_{10}-alkyl, C_1-C_{10}-halogenalkyl, C_1- C_{10}-cyanoalkyl, C_1- C_{10}-nitroalkyl, C_1- C_{10}-aminoalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7-cycloalkyl-C_1-C_5-alkyl, C_2- C_{10}-alkoxy-alkyl, C_4-C_{10}-alkenyloxy-alkyl, C_4- C_{10}-alkinyloxy-alkyl, C_2- C_{10}-alkylthio-alkyl, C_1-C_5-alkysulfoxyl- C_1-C_5-alkyl, C_1-C_5-alkylsulfonyl-C_1-C_5-alkyl, C_2-C_8-alkylideneamino-oxy-C_1-C_5-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_5-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_5-alkyl, C_1-C_5-amino-carbonyl-C_1-C_5-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_5-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_5-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_5-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl- C_1-C_5-alkyl, heteroaryl- C_1-C_5-alkyl, phenoxy- C_1-C_5-alkyl, heteroaryloxy- C_1-C_5-alkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, phenyl; or phenyl substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or heteroaryl or heteroarylamino; heteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-

alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diheteroarylamino, diheteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; phenylamino, phenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diphenylamino, diphenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkylamino, C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; di-C_3-C_7-cycloalkylamino, di-C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkoxy or C_3-C_7-cycloalkoxy substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_1-C_{10}-alkoxy, C_1-C_{10}-halogenalkoxy, C_1-C_5-alkylamino, C_2-C_8-dialkylamino as well as benzyloxy or phenoxy, whereby the benzyl and phenyl groups in turn may be substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano, formyl, acetyl, propionyl, carboxyl, C_1-C_5-alkoxycarbonyl, methylthio, ethylthio, or nitro; and

R_{37} is C_1-C_{10}-alkyl, C_1-C_{10}-halogenalkyl, C_1- C_{10}-cyanoalkyl, C_1- C_{10}-nitroalkyl, C_1- C_{10}-aminoalkyl, C_1-C_5-alkylamino-C_1-C_5-alkyl, C_2-C_8-dialkylamino- C_1-C_5-alkyl, C_3-C_7-cycialkyl-C_1-C_5-alkyl, C_2- C_{10}-alkoxy-alkyl, C_4- C_{10}-alkenyloxy-alkyl, C_4- C_{10}-alkinyloxy-alkyl, C_2- C_{10}-alkylthio-alkyl, C_1-C_5-alkysulfoxyl- C_1-C_5-alkyl, C_1-C_5-alkylsulfonyl-C_1-C_5-alkyl, C_2-C_8-alkylideneamino-oxy-C_1-C_5-alkyl, C_1-C_5-alkylcarbonyl-C_1-C_5-alkyl, C_1-C_5-alkoxycarbonyl-C_1-C_5-alkyl, C_1-C_5-amino-carbonyl-C_1-C_5-alkyl, C_2-C_8-dialkylamino-carbonyl-C_1-C_5-alkyl, C_1-C_5-alkylcarbonylamino-C_1-C_5-alkyl, C_2-C_5-alkylcarbonyl-(C_1-C_5-alkyl)-aminoalkyl, C_3-C_6-trialkylsilyl-C_1-C_5-alkyl, phenyl- C_1-C_5-alkyl, heteroaryl- C_1-C_5-alkyl, phenoxy- C_1-C_5-alkyl, heteroaryloxy- C_1-C_5-alkyl, C_2-C_5-alkenyl, C_2-C_5-halogenalkenyl, C_3-C_8-cycloalkyl, phenyl; or phenyl substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or heteroaryl or heteroarylamino; heteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diheteroarylamino, diheteroarylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; phenylamino, phenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; diphenylamino, diphenylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkylamino, C_3-C_7-cycloalkylamino substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; di-C_3-C_7-cycloalkylamino, di-C_3-C_7-cycloalkylamino

substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; C_3-C_7-cycloalkoxy or C_3-C_7-cycloalkoxy substituted by C_1-C_3-alkyl, C_1-C_3-halogenalkyl, C_1-C_3-alkoxy, C_1-C_3-halogenalkoxy, halogen, cyano or nitro; or C_1-C_{10}-alkylcarbonyl; as well as salts and diastereoisomers of the compounds of formula I, with the proviso that R_1 and R_3 are not simultaneously methyl; and;

b) a herbicidally synergistic amount of at least one herbicide selected from the classes of phenoxy-phenoxypropionic acids, hydroxylamines, sulfonylureas, imidazolinones, pyrimidines, triazines, ureas, PPO, chloroacetanilides, phenoxyacetic acids, triazinones, dinitroanilines, azinones, carbamates, oxyacetamides, thiolcarbamates, azole-ureas, benzoic acids, anilides, nitriles, triones and sulfonamides, as well as from the herbicides amitrol, benfuresate, bentazone, cinmethylin, clomazone, chlopyralid, difenzoquat, dithiopyr, ethofumesate, flurochloridone, indanofane, isoxaben, oxaziclomefone, pyridate, pyridafol, quinchlorac, quinmerac, tridiphane and flamprop.

2. Composition according to claim 1, which contains, to antagonise the herbicide, an antidotally effective amount of a safener selected from cloquintocet, an alkali, alkaline earth, sulfonium or ammonium cation of cloquintocet, cloquintocet-mexyl, mefenpyr, an alkali, alkaline earth, sulfonium or ammonium cation of mefenpyr and mefenpyr-diethyl.

3. Composition according to claim 1, which contains an additive comprising an oil of vegetable or animal origin, a mineral oil, the alkylesters thereof or mixtures of these oils and oil derivatives.

4. A method of selectively controlling weeds and grasses in crops of cultivated plants, which comprises treating said cultivated plants, the seeds or seedlings or the crop area thereof, with a composition according to claim 1.

5. A method of selectively controlling weeds and grasses in crops of cultivated plants, which comprises treating said cultivated plants, the seeds or seedlings or the crop area thereof, with a composition according to claim 2.

6. A method of selectively controlling weeds and grasses in crops of cultivated plants, which comprises treating said cultivated plants, the seeds or seedlings or the crop area thereof, with a composition according to claim 3.

7.A method according to claim 4 wherein the cultivated plant is cereal or maize.

INTERNATIONAL SEARCH REPORT

Interr. [redacted]pplication No
PCT/EP 00/08658

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N43/90 A01N25/32 //(A01N43/90,43:76,43:40,35:10,27:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 21652 A (CIBA GEIGY AG ;BOEGER MANFRED (DE); MAIENFISCH PETER (CH); CEDERBA) 18 July 1996 (1996-07-18) cited in the application page 1 -page 2, line 10 page 7, paragraph 3 page 16, last paragraph -page 18, paragraph 1 page 19, last paragraph -page 20, paragraph 1 page 30, paragraph 2 -page 31, paragraph 2 page 72, table 8; page 85, example B8 claims 1,40,57	1-7

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 December 2000	28/12/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Muellners, W

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inten [redacted] Application No
PCT/EP 00/08658

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 508 126 A (BAYER AG) 14 October 1992 (1992-10-14) page 3 -page 4, line 21 page 30, line 16 -page 31, line 40 pages 33-40, table 1 claims 1,3,4,11-14	1-7
P,A	WO 99 47525 A (NOVARTIS ERFINDUNGEN VERWALTUN ;MUEHLEBACH MICHEL (CH); GLOCK JUTT) 23 September 1999 (1999-09-23) page 1 -page 2, paragraph 1 page 19, paragraph 2 -page 20, paragraph 2 page 31, table 9; page 33, table 11 page 50, last paragraph -page 54 page 59, example H9; pages 62-67, table 1; pages 86-90, biological examples claims 1,14-18	1-7
A	DE 197 28 568 A (BAYER AG) 22 January 1998 (1998-01-22) page 2 -page 3, line 31 page 4, line 25 - line 32	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

information on patent family members

Inten Application No
PCT/EP 00/08658

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9621652 A	18-07-1996	AU 4435396 A	31-07-1996
		BR 9600088 A	27-01-1998
		CA 2210286 A	18-07-1996
		CN 1175248 A	04-03-1998
		EP 0804422 A	05-11-1997
		JP 10512248 T	24-11-1998
		TR 960702 A	21-08-1996
		ZA 9600243 A	19-08-1996
EP 0508126 A	14-10-1992	DE 4109208 A	24-09-1992
		BR 9200983 A	17-11-1992
		DE 59208415 D	05-06-1997
		ES 2101764 T	16-07-1997
		GR 3023621 T	29-08-1997
		JP 5117240 A	14-05-1993
		KR 212941 B	02-08-1999
		MX 9201103 A	21-12-1992
		US 5474974 A	12-12-1995
		US 5661110 A	26-08-1997
		US 5739389 A	14-04-1998
		US 5780394 A	14-07-1998
		US 5332720 A	26-07-1994
		US 5358924 A	25-10-1994
WO 9947525 A	23-09-1999	AU 3410999 A	11-10-1999
DE 19728568 A	22-01-1998	CA 2210273 A	17-01-1998
		FR 2751174 A	23-01-1998
		GB 2315413 A,B	04-02-1998
		US 5985797 A	16-11-1999